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(54) Title: DEEPLY REDUCED OXIDATION CATALYST AND ITS USE FOR CATALYZING LIQUID PHASE OXIDATION REACTIONS

(57) Abstract: This invention relates to an improved catalyst, comprising a carbon support having a noble metal at its surface, for use in catalyzing liquid phase oxidation reactions, especially in an acidic oxidative environment and in the presence of solvents, reactants, intermediates, or products which solubilize noble metals; a process for the preparation of the improved catalyst; a liquid phase oxidation process using such a catalyst wherein the catalyst exhibits improved resistance to noble metal leaching, particularly in acidic oxidative environments and in the presence of solvents, reactants, intermediates, or products which solubilize noble metals; and a liquid phase oxidation process in which N-(phosphonomethyl)iminodiacetic acid (i.e., "PMIDA") or a salt thereof is oxidized to form N-(phosphonomethyl)glycine (i.e., "glyphosate") or a salt thereof using such a catalyst wherein the oxidation of the formaldehyde and formic acid by-products into carbon dioxide and water is increased.

DEEPLY REDUCED OXIDATION CATALYST AND ITS USE FOR CATALYZING LIQUID PHASE OXIDATION REACTIONS
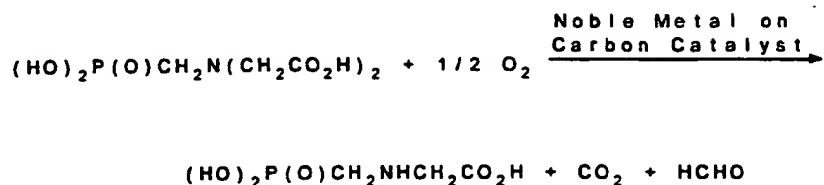
BACKGROUND OF THE INVENTION

This invention generally relates to an improved

5   oxidation catalyst and its use for catalyzing liquid
phase oxidation reactions, especially in acidic oxidative
environments and in the presence of reactants,
intermediates, products, or solvents which solubilize
noble metals. In a preferred embodiment, the present

10 invention relates to an improved oxidation catalyst and a
process in which the catalyst is used to convert
N-(phosphonomethyl)iminodiacetic acid or a salt thereof
into N-(phosphonomethyl)glycine or a salt thereof.

N-(phosphonomethyl)glycine (known in the

15 agricultural chemical industry as "glyphosate") is
described in Franz, U.S. Patent No. 3,799,758. N-
(phosphonomethyl)glycine and its salts are conveniently
applied as a post-emergent herbicide in an aqueous
formulation. It is a highly effective and commercially

20 important broad-spectrum herbicide useful in killing or
controlling the growth of a wide variety of plants,
including germinating seeds, emerging seedlings, maturing
and established woody and herbaceous vegetation, and
aquatic plants.

25 Various methods for making N-
(phosphonomethyl)glycine are known in the art. Franz
(U.S. Patent No. 3,950,402) teaches that N-
(phosphonomethyl)glycine may be prepared by the liquid
phase oxidative cleavage of

30 N-(phosphonomethyl)iminodiacetic acid (sometimes referred
to as "PMIDA") with oxygen in the presence of a catalyst

comprising a noble metal deposited on the surface of an

activated carbon support:

$$(HO)_2P(O)CH_2N(CH_2CO_2H)_2 \ + \ 1/2 \ O_2 \xrightarrow{\text{Noble Metal on Carbon Catalyst}}$$

$$(HO)_2P(O)CH_2NHCH_2CO_2H \ + \ CO_2 \ + \ HCHO$$

Other by-products also may form, such as formic acid,

5   which is formed by the oxidation of the formaldehyde by-

product; and aminomethylphosphonic acid ("AMPA"), which

is formed by the oxidation of N-(phosphonomethyl)glycine.

Even though the Franz method produces an acceptable yield

and purity of N-(phosphonomethyl)glycine, high losses of

10   the costly noble metal into the reaction solution (i.e.,

"leaching") result because under the oxidation conditions

of the reaction, some of the noble metal is oxidized into

a more soluble form and both PMIDA and N-

(phosphonomethyl)glycine act as ligands which solubilize

15   the noble metal.

         In U.S. Patent No. 3,969,398, Hershman teaches

that activated carbon alone, without the presence of a

noble metal, may be used to effect the oxidative cleavage

of PMIDA to form N-(phosphonomethyl)glycine. In U.S.

20   Patent Nos. 4,624,937, Chou further teaches that the

activity of the carbon catalyst taught by Hershman may be

increased by removing the oxides from the surface of the

carbon catalyst before using it in the oxidation

reaction. See also, U.S. Patent No. 4,696,772, which

25   provides a separate discussion by Chou regarding

increasing the activity of the carbon catalyst by

removing oxides from the surface of the carbon catalyst.

Although these processes obviously do not suffer from noble metal leaching, they do tend to produce greater concentrations of formaldehyde by-product when used to effect the oxidative cleavage of

5   N-phosphonomethyliminodiacetic acid. This formaldehyde by-product is undesirable because it reacts with N-(phosphonomethyl)glycine to produce unwanted by-products (mainly N-methyl-N-(phosphonomethyl)glycine, sometimes referred to as "NMG") which reduce the N-

10   (phosphonomethyl)glycine yield. In addition, the formaldehyde by-product itself is undesirable because of its potential toxicity. <u>See</u> Smith, U.S. Patent No. 5,606,107.

         Optimally, therefore, it has been suggested

15   that the formaldehyde be simultaneously oxidized to carbon dioxide and water as the PMIDA is oxidized to N-(phosphonomethyl)glycine in a single reactor, thus giving the following reaction:

$$(HO)_2P(O)CH_2N(CH_2CO_2H)_2 \xrightarrow{Catalyst + O_2}$$

$$(HO)_2P(O)CH_2NHCH_2CO_2H + 2CO_2 + H_2O$$
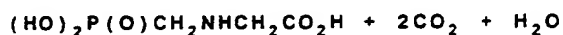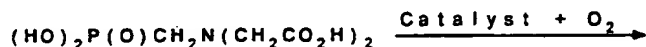
20   As the above teachings suggest, such a process requires the presence of both carbon (which primarily effects the oxidation of PMIDA to form N-(phosphonomethyl)glycine and formaldehyde) and a noble metal (which primarily effects the oxidation of formaldehyde to form carbon dioxide and

25   water). Previous attempts to develop a stable catalyst for such an oxidation process, however, have not been entirely satisfactory.

Like Franz, Ramon et al. (U.S. Patent No.
5,179,228) teach using a noble metal deposited on the
surface of a carbon support. To reduce the problem of
leaching (which Ramon et al. report to be as great as 30%

5   noble metal loss per cycle), however, Ramon et al. teach
flushing the reaction mixture with nitrogen under
pressure after the oxidation reaction is completed to
cause re-deposition of the noble metal onto the surface
of the carbon support. According to Ramon et al.,

10   nitrogen flushing reduces the noble metal loss to less
than 1%. Still, the amount of noble metal loss incurred
with this method is unacceptable. In addition, re-
depositing the noble metal can lead to loss of noble
metal surface area which, in turn, decreases the activity

15   of the catalyst.

Using a different approach, Felthouse (U.S.
Patent No. 4,582,650) teaches using two catalysts: (i)
an activated carbon to effect the oxidation of PMIDA into
N-(phosphonomethyl)glycine, and (ii) a co-catalyst to

20   concurrently effect the oxidation of formaldehyde into
carbon dioxide and water. The co-catalyst consists of an
aluminosilicate support having a noble metal located
within its pores. The pores are sized to exclude N-
(phosphonomethyl)glycine and thereby prevent the noble

25   metal of the co-catalyst from being poisoned by N-
(phosphonomethyl)glycine. According to Felthouse, use of
these two catalysts together allows for the simultaneous
oxidation of PMIDA to N-(phosphonomethyl)glycine and of
formaldehyde to carbon dioxide and water. This approach,

30   however, suffers from several disadvantages: (1) it is
difficult to recover the costly noble metal from the

4

aluminosilicate support for re-use; (2) it is difficult
to design the two catalysts so that the rates between
them are matched; and (3) the carbon support, which has
no noble metal deposited on its surface, tends to
5 deactivate at a rate which can exceed 10% per cycle.

    Thus, a need exists for an improved, multi-
reaction catalyst and reaction process which oxidizes
PMIDA to N-(phosphonomethyl)glycine while simultaneously
exhibiting resistance to noble metal leaching and
10 increased oxidation of formaldehyde into carbon dioxide
and water (_i.e._, increased formaldehyde activity).

SUMMARY OF THE INVENTION

    This invention provides for an improved
catalyst for use in catalyzing liquid phase oxidation
15 reactions, especially in an acidic oxidative environment
and in the presence of solvents, reactants,
intermediates, or products which solubilize noble metals;
a process for the preparation of the improved catalyst; a
liquid phase oxidation process using such a catalyst
20 wherein the catalyst exhibits improved resistance to
noble metal leaching, particularly in acidic oxidative
environments and in the presence of solvents, reactants,
intermediates, or products which solubilize noble metals;
and a liquid phase oxidation process in which PMIDA or a
25 salt thereof is oxidized to form N-
(phosphonomethyl)glycine or a salt thereof using such a
catalyst wherein the oxidation of the formaldehyde by-
product into carbon dioxide and water is increased.

    Briefly, therefore, the present invention is
30 directed to a novel oxidation catalyst comprising a

carbon support having a noble metal at its surface. In
one embodiment, the catalyst is characterized as yielding
no more than about 0.7 mmole of carbon monoxide per gram
of catalyst when a dry sample of the catalyst in a helium
5   atmosphere is heated from about 20 to about 900°C at a
rate of about 10°C per minute, and then at about 900°C
for about 30 minutes.

In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
10   at its surface, the carbon support also has a promoter at
the surface. The catalyst is characterized as yielding
no more than about 0.7 mmole of carbon monoxide per gram
of catalyst when a dry sample of the catalyst, after
being heated at a temperature of about 500°C for about 1
15   hour in a hydrogen atmosphere and before being exposed to
an oxidant following the heating in the hydrogen
atmosphere, is heated in a helium atmosphere from about
20 to about 900°C at a rate of about 10°C per minute, and
then at about 900°C for about 30 minutes.

20   In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
at its surface, the support also has carbon and oxygen at
the surface. The ratio of carbon atoms to oxygen atoms
at the surface is at least about 30:1 as measured by x-
25   ray photoelectron spectroscopy.

In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
at its surface, the support also has a promoter, carbon,
and oxygen at the surface. The catalyst is characterized
30   as having a ratio of carbon atoms to oxygen atoms of at
least about 30:1 at the surface as measured by x-ray

photoelectron spectroscopy after the catalyst is heated
at a temperature of about 500°C for about 1 hour in a
hydrogen atmosphere and before the catalyst is exposed to
an oxidant following the heating in the hydrogen
5   atmosphere.

In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
at its surface, the support also has a surface layer
which has a thickness of about 50 Å as measured inwardly
10   from the surface. This surface layer comprises oxygen
and carbon, with the ratio of carbon atoms to oxygen
atoms in the surface layer being at least about 30:1.

In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
15   at its surface, the support also has a promoter at the
surface. In addition, the support has a surface layer
having a thickness of about 50 Å as measured inwardly
from the surface and comprising carbon and oxygen. In
this embodiment, the catalyst is characterized as having
20   a ratio of carbon atoms to oxygen atoms in the surface
layer of least about 30:1 as measured by x-ray
photoelectron spectroscopy after the catalyst is heated
at a temperature of about 500°C for about 1 hour in a
hydrogen atmosphere and before the catalyst is exposed to
25   an oxidant following the heating in the hydrogen
atmosphere.

In another embodiment directed to an oxidation
catalyst comprising a carbon support having a noble metal
at its surface, the catalyst is prepared by a process
30   comprising depositing a noble metal at the surface, and

then heating the surface at a temperature greater than about 500°C.

In another embodiment directed to an oxidation catalyst comprising a carbon support having a noble metal at its surface, the catalyst is prepared by a process comprising depositing a noble metal at the surface, and then heating the surface at a temperature of at least about 400°C. In this embodiment, before the noble metal deposition, the carbon support has carbon and oxygen at its surface in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

In another embodiment directed to an oxidation catalyst comprising a carbon support having a noble metal at its surface, the catalyst is prepared by a process comprising depositing a noble metal at the surface, and then exposing the surface to a reducing environment. Here again, before the noble metal deposition, the carbon support has carbon and oxygen at its surface in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

This invention is also directed to a process for the preparation of an oxidation catalyst. In one embodiment of this invention, the process comprises depositing a noble metal at a surface of a carbon support, and then heating the surface at a temperature greater than about 500°C.

In another embodiment directed to a process for the preparation of an oxidation catalyst, the catalyst is prepared from a carbon support having carbon and oxygen

at a surface of the carbon support. The process comprises depositing a noble metal at the surface of the carbon support, and then heating the surface at a temperature of at least about 400°C. In this embodiment,

5 before the noble metal deposition, the ratio of carbon atoms to oxygen atoms at the surface of the carbon support is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

In another embodiment directed to a process for

10 the preparation of an oxidation catalyst, the catalyst is prepared from a carbon support having carbon and oxygen at a surface of the carbon support. The process comprises depositing a noble metal at the surface of the carbon support, and then exposing the surface to a

15 reducing environment. In this embodiment, before the noble metal deposition, the ratio of carbon atoms to oxygen atoms at the surface of the carbon support is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

20 In another embodiment directed to a process for the preparation of an oxidation catalyst, the catalyst is prepared from a carbon support having carbon and oxygen at a surface of the carbon support. The process comprises depositing a noble metal at the surface, and

25 then exposing the surface to a reducing environment to reduce the surface so that the ratio of carbon atoms to oxygen atoms at the surface is at least about 30:1 as measured by x-ray photoelectron spectroscopy.

In another embodiment directed to a process for

30 the preparation of an oxidation catalyst, the process comprises depositing a noble metal at a surface of a

carbon support, and then exposing the surface to a reducing environment to reduce the surface so that no more than about 0.7 mmole of carbon monoxide per gram of catalyst desorb from the catalyst when a dry sample of

5   the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

        This invention is also directed to a process for oxidizing a reagent in a mixture (typically a

10   solution or a slurry, and most typically a solution), wherein the mixture has the ability to solubilize a noble metal. This process comprises contacting the mixture with an oxidation catalyst in the presence of oxygen. In one embodiment, the catalyst comprises a carbon support

15   having a noble metal at its surface. The catalyst is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and

20   then at about 900°C for about 30 minutes.

        In another·embodiment directed to the process for oxidizing a reagent in a mixture which can solubilize a noble metal, the catalyst comprises a carbon support having a noble metal and a promoter at a surface of the

25   carbon support. In addition, the catalyst is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst, after being heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and

30   before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium

atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

In another embodiment directed to the process for oxidizing a reagent in a mixture which can solubilize a noble metal, the catalyst comprises a carbon support having a noble metal, carbon, and oxygen at a surface of the carbon support. The ratio of carbon atoms to oxygen atoms at the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

In another embodiment directed to the process for oxidizing a reagent in a mixture which can solubilize a noble metal, the catalyst comprises a carbon support having a noble metal, a promoter, carbon, and oxygen at a surface of the carbon support. The catalyst is characterized as having a ratio of carbon atoms to oxygen atoms at the surface which is at least about 20:1 as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

In another embodiment directed to the process for oxidizing a reagent in a mixture which can solubilize a noble metal, the catalyst comprises a carbon support having a noble metal at a surface of the carbon support. In addition, the support comprises a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising oxygen and carbon. The ratio of carbon atoms to oxygen atoms in the surface layer is at

least about 20:1 as measured by x-ray photoelectron
spectroscopy.

In another embodiment directed to the process
for oxidizing a reagent in a mixture which can solubilize
5 a noble metal, the catalyst comprises a carbon support
having: (a) a noble metal and a promoter at a surface of
the carbon support; and (b) a surface layer having a
thickness of about 50 Å as measured inwardly from the
surface and comprising carbon and oxygen. The catalyst
10 is characterized as having a ratio of carbon atoms to
oxygen atoms in the surface layer of at least about 20:1
as measured by x-ray photoelectron spectroscopy after the
catalyst is heated at a temperature of about 500°C for
about 1 hour in a hydrogen atmosphere and before the
15 catalyst is exposed to an oxidant following the heating
in the hydrogen atmosphere.

In another embodiment directed to the process
for oxidizing a reagent in a mixture which can solubilize
a noble metal, the catalyst is prepared by a process
20 comprising depositing a noble metal at a surface of a
carbon support, and then heating the surface at a
temperature of at least about 400°C.

In another embodiment directed to the process
for oxidizing a reagent in a mixture which can solubilize
25 a noble metal, the catalyst is prepared by a process
comprising depositing a noble metal at a surface of a
carbon support, and then exposing the surface to a
reducing environment. In this embodiment, before the
noble metal deposition, the carbon support has carbon and
30 oxygen at the surface of the carbon support in amounts
such that the ratio of carbon atoms to oxygen atoms at

the surface is at least 20:1 as measured by x-ray
photoelectron spectroscopy.

This invention is further directed to a process
for the preparation of N-(phosphonomethyl)glycine or a

5   salt thereof. The process comprises contacting N-
(phosphonomethyl)iminodiacetic acid or a salt thereof
with an oxidation catalyst in the presence of oxygen. In
one embodiment, the catalyst comprises a carbon support
having a noble metal at a surface of the carbon support.

10   The catalyst is characterized as yielding no more than
about 1.2 mmole of carbon monoxide per gram of catalyst
when a dry sample of the catalyst in a helium atmosphere
is heated from about 20 to about 900°C at a rate of about
10°C per minute, and then at about 900°C for about 30

15   minutes.

In another embodiment directed to the process
for the preparation of N-(phosphonomethyl)glycine or a
salt thereof, the catalyst comprises a carbon support
having a noble metal, carbon, and oxygen at a surface of

20   the carbon support. The ratio of carbon atoms to oxygen
atoms at the surface is at least about 20:1 as measured
by x-ray photoelectron spectroscopy.

In another embodiment directed to the process
for the preparation of N-(phosphonomethyl)glycine or a

25   salt thereof, the catalyst comprises a carbon support
having a noble metal at a surface of the carbon support.
The carbon support also comprises a surface layer having
a thickness of about 50 Å as measured inwardly from the
surface and comprising carbon and oxygen. The ratio of

30   carbon atoms to oxygen atoms in the surface layer is at

13

least about 20:1 as measured by x-ray photoelectron spectroscopy.

　　　　　In another embodiment directed to the process for the preparation of N-(phosphonomethyl)glycine or a
5　salt thereof, the catalyst is prepared by a process comprising depositing a noble metal at a surface of a carbon support, and then heating the surface at a temperature of at least about 400°C.

　　　　　In another embodiment directed to the process
10　for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the catalyst is prepared by a process comprising depositing a noble metal at a surface of a carbon support, and then exposing the surface to a reducing environment. In this embodiment, before the
15　noble metal deposition, the carbon support has carbon and oxygen at its surface in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least 20:1 as measured by x-ray photoelectron spectroscopy.

　　　　　In another embodiment directed to the process
20　for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the catalyst comprises a carbon support having a noble metal, a promoter, carbon, and oxygen at a surface of the carbon support.

　　　　　In another embodiment directed to the process
25　for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the catalyst comprises a carbon support having a noble metal and a promoter at a surface of the carbon support. The catalyst also comprises a surface layer having a thickness of about 50 Å as measured
30　inwardly from the surface. This surface layer comprises carbon and oxygen. In this embodiment, the catalyst is

14

characterized as having a ratio of carbon atoms to oxygen
atoms in the surface layer which is at least about 20:1
as measured by x-ray photoelectron spectroscopy after the
catalyst is heated at a temperature of about 500°C for
5   about 1 hour a hydrogen atmosphere and before the
catalyst is exposed to an oxidant following the heating
in the hydrogen atmosphere.

       Other features of this invention will be in
part apparent and in part pointed out hereinafter.

10   BRIEF DESCRIPTION OF THE DRAWINGS

       Figure 1 is a TEM image of an oxidation
catalyst comprising a carbon support having platinum
alloyed with iron at the surface of the carbon support.

       Figure 2 is a high energy resolution X-ray
15   spectra from an individual metal particle of an oxidation
catalyst comprising a carbon support having platinum
alloyed with iron at the surface of the carbon support.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A.   **The oxidation catalyst**

20   The catalyst of the present invention may be
used to catalyze liquid phase (i.e., in an aqueous
solution or an organic solvent) oxidation reactions,
especially in acidic oxidative environments and in the
presence of solvents, reactants, intermediates, or
25   products which solubilize noble metals. The catalyst
exhibits significantly improved resistance to noble metal
leaching under these conditions. Advantageously, the
catalyst additionally exhibits an improved oxidation
(i.e., destruction) of the formaldehyde and formic acid

15

by-products during the oxidation of PMIDA to N-(phosphonomethyl)glycine.

The noble metal component of the catalyst serves various functions. For example, depositing a
5　noble metal onto the surface of a catalyst consisting of a carbon support alone tends to reduce the rate of deactivation of the catalyst. To illustrate, when N-(phosphonomethyl)glycine is prepared by the liquid phase oxidative cleavage of PMIDA with oxygen in the presence
10　of a catalyst consisting of an activated carbon support without a noble metal, the activated carbon is found to deactivate as much as 10% per cycle or more. Without being bound by any particular theory, it is believed that the deactivation of the activated carbon arises because
15　the surface of the carbon support oxidizes under the reaction conditions. See Chou, U.S. Patent No. 4,624,937. See also, Chou, U.S. Patent No. 4,696,772, which provides a separate discussion related to deactivation of activated carbon by oxidation of the
20　surface of the carbon. In the presence of the noble metal, however, the rate of deactivation of the activated carbon is diminished. It is believed that the noble metal can react with the oxidant at a faster rate than the activated carbon surface and thus preferentially
25　removes the oxidant from solution before extensive oxidation of the carbon surface can occur. Further, unlike many oxide species which form at activated carbon surfaces and require high temperature treatments to be reduced, oxide species which form at the surface of a
30　noble metal typically are easily reduced by the reducing agents present in or added to the reaction mixture (e.g.,

16

the amine fragment cleaved, formaldehyde, formic acid, H_2, etc.), thus restoring the noble metal surface to a reduced state. In this manner, the catalyst of this invention advantageously exhibits significantly longer

5   life as long as the noble metal is not lost by leaching, or sintered (i.e., in the form of undesirably thick layers or clumps) by processes such as dissolution and re-deposition or noble metal agglomeration.

        Also, depending on the particular oxidation

10   reaction, a noble metal may be more effective than carbon at effecting the oxidation. For example, in the context of the oxidative cleavage of PMIDA to form N-(phosphonomethyl)glycine, although the carbon component of the catalyst primarily effects the oxidation of PMIDA

15   to N-(phosphonomethyl)glycine, it is the noble metal component that primarily effects the oxidation of the undesirable formaldehyde and formic acid by-products into the more preferred by-products, carbon dioxide and water.

        It has been discovered in accordance with this

20   invention that oxygen-containing functional groups (e.g., carboxylic acids, ethers, alcohols, aldehydes, lactones, ketones, esters, amine oxides, and amides) at the surface of the carbon support increase noble metal leaching and potentially increase noble metal sintering during liquid

25   phase oxidation reactions and thus reduce the ability of the catalyst to oxidize oxidizable substrates, particularly formaldehyde during the PMIDA oxidation reaction. As used herein, an oxygen-containing functional group is "at the surface of the carbon

30   support" if it is bound to an atom of the carbon support and is able to chemically or physically interact with

17

compositions within the reaction mixture or with the metal atoms deposited on the carbon support.

Many of the oxygen-containing functional groups that reduce noble metal resistance to leaching and

5   sintering and reduce the activity of the catalyst desorb from the carbon support as carbon monoxide when the catalyst is heated at a high temperature (e.g., 900°C) in an inert atmosphere (e.g., helium or argon). Thus, measuring the amount of CO desorption from a fresh

10 catalyst (i.e., a catalyst that has not previously been used in a liquid phase oxidation reaction) under high temperatures is one method that may be used to analyze the surface of the catalyst to predict noble metal retention and maintenance of catalyst activity. One way

15 to measure CO desorption is by using thermogravimetric analysis with in-line mass spectroscopy ("TGA-MS"). Preferably, no more than about 1.2 mmole of carbon monoxide per gram of catalyst desorb from the catalyst when a dry, fresh sample of the catalyst in a helium

20 atmosphere is subjected to a temperature which is increased from about 20 to about 900°C at about 10°C per minute, and then held constant at about 900°C for about 30 minutes. More preferably, no more than about 0.7 mmole of carbon monoxide per gram of fresh catalyst

25 desorb under those conditions, even more preferably no more than about 0.5 mmole of carbon monoxide per gram of fresh catalyst desorb, and most preferably no more than about 0.3 mmole of carbon monoxide per gram of fresh catalyst desorb. A catalyst is considered "dry" when the

30 catalyst has a moisture content of less than about 1% by weight. Typically, a catalyst may be dried by placing it

18

into a N$_2$ purged vacuum of about 25 inches of Hg and a
temperature of about 120°C for about 16 hours.

Measuring the number of oxygen atoms at the
surface of a fresh catalyst support is another method
5   which may be used to analyze the catalyst to predict
noble metal retention and maintenance of catalytic
activity. Using, for example, x-ray photoelectron
spectroscopy, a surface layer of the support which is
about 50 Å in thickness is analyzed. Presently available
10 equipment used for x-ray photoelectron spectroscopy
typically is accurate to within ±20%. Typically, a ratio
of carbon atoms to oxygen atoms at the surface (as
measured by presently available equipment for x-ray
photoelectron spectroscopy) of at least about 20:1
15 (carbon atoms:oxygen atoms) is suitable. Preferably,
however, the ratio is at least about 30:1, more
preferably at least about 40:1, even more preferably at
least about 50:1, and most preferably at least about
60:1. In addition, the ratio of oxygen atoms to metal
20 atoms at the surface (again, as measured by presently
available equipment for x-ray photoelectron spectroscopy)
preferably is less than about 8:1 (oxygen atoms:metal
atoms). More preferably, the ratio is less than 7:1,
even more preferably less than about 6:1, and most
25 preferably less than about 5:1.

In general, the carbon supports used in the
present invention are well known in the art. Activated,
non-graphitized carbon supports are preferred. These
supports are characterized by high adsorptive capacity
30 for gases, vapors, and colloidal solids and relatively
high specific surface areas. The support suitably may be

19

a carbon, char, or charcoal produced by means known in the art, for example, by destructive distillation of wood, peat, lignite, coal, nut shells, bones, vegetable, or other natural or synthetic carbonaceous matter, but

5 preferably is "activated" to develop adsorptive power. Activation usually is achieved by heating to high temperatures (800 - 900°C) with steam or with carbon dioxide which brings about a porous particle structure and increased specific surface area. In some cases,

10 hygroscopic substances, such as zinc chloride and/or phosphoric acid or sodium sulfate, are added before the destructive distillation or activation, to increase adsorptive capacity. Preferably, the carbon content of the carbon support ranges from about 10% for bone

15 charcoal to about 98% for some wood chars and nearly 100% for activated carbons derived from organic polymers. The non-carbonaceous matter in commercially available activated carbon materials normally will vary depending on such factors as precursor origin, processing, and

20 activation method. Many commercially available carbon supports contain small amounts of metals. Carbon supports having the fewest oxygen-containing functional groups at their surfaces are most preferred.

The form of the carbon support is not critical.

25 In one embodiment of this invention, the support is a monolithic support. Suitable monolithic supports may have a wide variety of shapes. Such a support may be, for example, in the form of a screen or honeycomb. Such a support may also, for example, be in the form of a

30 reactor impeller.

20

In a particularly preferred embodiment, the support are in the form of particulates. Because particulate supports are especially preferred, most of the following discussion focuses on embodiments which use a particulate support. It should be recognized, however, that this invention is not limited to the use of particulate supports.

Suitable particulate supports may have a wide variety of shapes. For example, such supports may be in the form of granules. Even more preferably, the support is in the form of a powder. These particulate supports may be used in a reactor system as free particles, or, alternatively, may be bound to a structure in the reactor system, such as a screen or an impeller.

Typically, a support which is in particulate form comprises a broad size distribution of particles. For powders, preferably at least about 95% of the particles are from about 2 to about 300 μm in their largest dimension, more preferably at least about 98% of the particles are from about 2 to about 200 μm in their largest dimension, and most preferably about 99% of the particles are from about 2 to about 150 μm in their largest dimension with about 95% of the particles being from about 3 to about 100 μm in their largest dimension. Particles being greater than about 200 μm in their largest dimension tend to fracture into super-fine particles (i.e., less than 2 μm in their largest dimension), which are difficult to recover.

The specific surface area of the carbon support, measured by the BET (Brunauer-Emmett-Teller) method using N_2, is preferably from about 10 to about

21

3,000 m²/g (surface area of carbon support per gram of
carbon support), more preferably from about 500 to about
2,100 m²/g, and still more preferably from about 750 to
about 2,100 m²/g. In some embodiments, the most preferred
5   specific area is from about 750 to about 1,750 m²/g.

The pore volume of the support may vary widely.
Using the measurement method described in Example 1, the
pore volume preferably is from about 0.1 to about 2.5
ml/g (pore volume per gram of catalyst), more preferably
10   from about 0.2 to about 2.0 ml/g, and most preferably
from about 0.4 to about 1.7 ml/g. Catalysts comprising
supports with pore volumes greater than about 2.5 ml/g
tend to fracture easily. On the other hand, catalysts
comprising supports having pore volumes less than 0.1
15   ml/g tend to have small surface areas and therefore low
activity.

Carbon supports for use in the present
invention are commercially available from a number of
sources. The following is a listing of some of the
20   activated carbons which may be used with this invention:
Darco G-60 Spec and Darco X (ICI-America, Wilmington,
DE); Norit SG Extra, Norit EN4, Norit EXW, Norit A, Norit
Ultra-C, Norit ACX, and Norit 4 X 14 mesh (Amer. Norit
Co., Inc., Jacksonville, FL); Gl-9615, VG-8408, VG-8590,
25   NB-9377, XZ, NW, and JV (Barnebey-Cheney, Columbus, OH);
BL Pulv., PWA Pulv., Calgon C 450, and PCB Fines
(Pittsburgh Activated Carbon, Div. of Calgon Corporation,
Pittsburgh, PA); P-100 (No. Amer. Carbon, Inc., Columbus,
OH); Nuchar CN, Nuchar C-1000 N, Nuchar C-190 A, Nuchar
30   C-115 A, and Nuchar SA-30 (Westvaco Corp., Carbon
Department, Covington, Virginia); Code 1551 (Baker and

22

Adamson, Division of Allied Amer. Norit Co., Inc.,

Jacksonville, FL); Grade 235, Grade 337, Grade 517, and

Grade 256 (Witco Chemical Corp., Activated Carbon Div.,

New York, NY); and Columbia SXAC (Union Carbide New York,

5   NY).

The catalyst of this invention preferably has

one or more noble metal(s) at its surface. Preferably,

the noble metal(s) is selected from the group consisting

of platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium

10 (Rh), iridium (Ir), silver (Ag), osmium (Os), and gold

(Au). In general, platinum and palladium are more

preferred, and platinum is most preferred. Because

platinum is presently the most preferred noble metal, the

following discussion will be directed primarily to

15 embodiments using platinum. It should be understood,

however, that the same discussion is generally applicable

to the other noble metals and combinations thereof. It

also should be understood that the term "noble metal" as

used herein means the noble metal in its elemental state

20 as well as the noble metal in any of its various

oxidation states.

The concentration of the noble metal deposited

at the surface of the carbon support may vary within wide

limits. Preferably, it is in the range of from about 0.5

25 to about 20 wt.% ([mass of noble metal ÷ total mass of

catalyst] x 100%), more preferably from about 2.5 to

about 10 wt.%, and most preferably from about 3 to about

7.5 wt.%. If concentrations less than 0.5 wt.% are used

during the PMIDA oxidation reaction, there tends to be

30 less formaldehyde oxidized, and therefore a greater

amount of NMG produced, ther by reducing the N-

23

(phosphonomethyl)glycine yield. On the other hand, at
concentrations greater than about 20 wt.%, layers and
clumps of noble metal tend to form. Thus, there are
fewer surface noble metal atoms per total amount of noble

5   metal used. This tends to reduce the activity of the
catalyst and is an uneconomical use of the costly noble
metal.

The dispersion of the noble metal at the
surface of the carbon support preferably is such that the

10 concentration of surface noble metal atoms is from about
10 to about 400 μmole/g (μmole of surface noble metal
atoms per gram of catalyst), more preferably, from about
10 to about 150 μmole/g, and most preferably from about
15 to about 100 μmole/g. This may be determined, for

15 example, by measuring chemisorption of H_2 or CO using a
Micromeritics ASAP 2010C (Micromeritics, Norcross, GA) or
an Altamira AMI100 (Zeton Altamira, Pittsburgh, PA).

Preferably, the noble metal is at the surface
of the carbon support in the form of metal particles. At

20 least about 90% (number density) of the noble metal
particles at the surface of the carbon support are
preferably from about 0.5 to about 35 nm in their largest
dimension, more preferably from about 1 to about 20 nm in
their largest dimension, and most preferably from about

25 1.5 to about 10 nm in their largest dimension. In a
particularly preferred embodiment, at least about 80% of
the noble metal particles at the surface of the carbon
support are from about 1 to about 15 nm in their largest
dimension, more preferably from about 1.5 to about 10 nm

30 in their largest dimension, and most preferably from
about 1.5 to about 7 nm in their largest dimension. If

24

the noble metal particles are too small, there tends to
be an increased amount of leaching when the catalyst is
used in an environment that tends to solubilize noble
metals, as is the case when oxidizing PMIDA to form N-
5   (phosphonomethyl)glycine. On the other hand, as the
particle size increases, there tends to be fewer noble
metal surface atoms per total amount of noble metal used.
As discussed above, this tends to reduce the activity of
the catalyst and is also an uneconomical use of the
10   costly noble metal.

        In addition to the noble metal, at least one
promoter may be at the surface of the carbon support.
Although the promoter typically is deposited onto the
surface of the carbon support, other sources of promoter
15   may be used (e.q., the carbon support itself may
naturally contain a promoter). A promoter tends to
increase catalyst selectivity, activity, and/or
stability. A promoter additionally may reduce noble
metal leaching.

20   The promoter may, for example, be an additional
noble metal(s) at the surface of the carbon support. For
example, ruthenium and palladium have been found to act
as promoters on a catalyst comprising platinum deposited
at a carbon support surface. The promoter(s)
25   alternatively may be, for example, a metal selected from
the group consisting of tin (Sn), cadmium (Cd), magnesium
(Mg), manganese (Mn), nickel (Ni), aluminum (Al), cobalt
(Co), bismuth (Bi), lead (Pb), titanium (Ti), antimony
(Sb), selenium (Se), iron (Fe), rhenium (Re), zinc (Zn),
30   cerium (Ce), and zirconium (Zr). Preferably, the
promoter is selected from the group consisting of

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bismuth, iron, tin, and titanium. In a particularly
preferred embodiment, the promoter is tin. In another
particularly preferred embodiment, the promoter is iron.
In an additional preferred embodiment, the promoter is

5   titanium. In a further particularly preferred
embodiment, the catalyst comprises both iron and tin.
Use of iron, tin, or both generally (1) reduces noble
metal leaching for a catalyst used over several cycles,
and (2) tends to increase and/or maintain the activity of

10 the catalyst when the catalyst is used to effect the
oxidation of PMIDA. Catalysts comprising iron generally
are most preferred because they tend to have the greatest
activity and stability with respect to formaldehyde and
formic acid oxidation.

15   In one preferred embodiment, the promoter is
more easily oxidized than the noble metal. A promoter is
"more easily oxidized" if it has a lower first ionization
potential than the noble metal. First ionization
potentials for the elements are widely known in the art

20 and may be found, for example, in the CRC Handbook of
Chemistry and Physics (CRC Press, Inc., Boca Raton,
Florida).

            The amount of promoter at the surface of the
carbon support (whether associated with the carbon

25 surface itself, metal, or a combination thereof) may vary
within wide limits depending on, for example, the noble
metal and promoter used. Typically, the weight
percentage of the promoter is at least about 0.05% ([mass
of promoter ÷ total mass of the catalyst] X 100%). The

30 weight percent of the promoter preferably is from about
0.05 to about 10%, more preferably from about 0.1 to

about 10%, still more preferably from about 0.1 to about
2%, and most preferably from about 0.2 to about 1.5%.
When the promoter is tin, the weight percent most
preferably is from about 0.5 to about 1.5%. Promoter
5   weight percentages less than 0.05% generally do not
promote the activity of the catalyst over an extended
period of time. On the other hand, weight percents
greater than about 10% tend to decrease the activity of
the catalyst.

10   The molar ratio of noble metal to promoter may
also vary widely, depending on, for example, the noble
metal and promoter used. Preferably, the ratio is from
about 1000:1 to about 0.01:1; more preferably from about
150:1 to about 0.05:1; still more preferably from about
15   50:1 to about 0.05:1; and most preferably from about 10:1
to about 0.05:1. For example, a catalyst comprising
platinum and iron preferably has a molar ratio of
platinum to iron of about 3:1.

         In a particularly preferred embodiment of this
20   invention, the noble metal (e.g., Pt) is alloyed with at
least one promoter (e.g., Sn, Fe, or both) to form
alloyed metal particles. A catalyst comprising a noble
metal alloyed with at least one promoter tends to have
all the advantages discussed above with respect to
25   catalysts comprising a promoter. It has been found in
accordance with this invention, however, that catalysts
comprising a noble metal alloyed with at least one
promoter tend to exhibit greater resistance to promoter
leaching and further stability from cycle to cycle with
30   respect to formaldehyde and formic acid oxidation. See,
e.g., Example 17.

27

The term "alloy" encompasses any metal particle comprising a noble metal and at least one promoter, irrespective of the precise manner in which the noble metal and promoter atoms are disposed within the particle

5   (although it is generally preferable to have a portion of the noble metal atoms at the surface of the alloyed metal particle). The alloy may be, for example, any of the following:

1.   An intermetallic compound. An intermetallic

10   compound is compound comprising a noble metal and a promoter (e.g., Pt$_3$Sn).

2.   A substitutional alloy. A substitutional alloy has a single, continuous phase, irrespective of the concentrations of the noble metal and

15   promoter atoms. Typically, a substitutional alloy contains noble metal and promoter atoms which are similar in size (e.g., platinum and silver; or platinum and palladium). Substitutional alloys are also referred to as

20   "monophasic alloys."

3.   A multiphasic alloy. A multiphasic alloy is an alloy that contains at least two discrete phases. Such an alloy may contain, for example Pt$_3$Sn in one phase, and tin dissolved in

25   platinum in a separate phase.

4.   A segregated alloy. A segregated alloy is a metal particle wherein the particle stoichiometry varies with distance from the surface of the metal particle.

30   5.   An interstitial alloy. An interstitial alloy is a metal particle wherein the noble metal and

28

promoter atoms are combined with non-metal
atoms, such as boron, carbon, silicon,
nitrogen, phosphorus, etc.

Preferably, at least about 80% (number density)
5   of the alloyed metal particles are from about 0.5 to
about 35 nm in their largest dimension, more preferably
from about 1 to about 20 nm in their largest dimension,
still more preferably from about 1 to about 15 nm in
their largest dimension, and most preferably from about
10   1.5 to about 7 nm in their largest dimension.

The alloyed metal particles need not have a
uniform composition; the compositions may vary from
particle to particle, or even within the particles
themselves. In addition, the catalyst may further
15   comprise particles consisting of the noble metal alone or
the promoter alone. Nevertheless, it is preferred that
the composition of metal particles be substantially
uniform from particle to particle and within each
particle, and that the number of noble metal atoms in
20   intimate contact with promoter atoms be maximized. It is
also preferred, although not essential, that the majority
of noble metal atoms be alloyed with a promoter, and more
preferred that substantially all of the noble metal atoms
be alloyed with a promoter. It is further preferred,
25   although not essential, that the alloyed metal particles
be uniformly distributed at the surface of the carbon
support.

Regardless of whether the promoter is alloyed
to the noble metal, it is presently believed that the
30   promoter tends to become oxidized if the catalyst is
exposed to an oxidant over a period of time. For

29

example, an elemental tin promoter tends to oxidize to form $Sn(II)O$, and $Sn(II)O$ tends to oxidize to form $Sn(IV)O_2$. This oxidation may occur, for example, if the catalyst is exposed to air for more than about 1 hour.

5 Although such promoter oxidation has not been observed to have a significant detrimental effect on noble metal leaching, noble metal sintering, catalyst activity, or catalyst stability, it does make analyzing the concentration of detrimental oxygen-containing functional

10 groups at the surface of the carbon support more difficult. For example, as discussed above, the concentration of detrimental oxygen-containing functional groups (i.e., oxygen-containing functional groups that reduce noble metal resistance to leaching and sintering,

15 and reduce the activity of the catalyst) may be determined by measuring (using, for example, TGA-MS) the amount of CO that desorbs from the catalyst under high temperatures in an inert atmosphere. However, it is presently believed that when an oxidized promoter is

20 present at the surface, the oxygen atoms from the oxidized promoter tend to react with carbon atoms of the support at high temperatures in an inert atmosphere to produce CO, thereby creating the illusion of more detrimental oxygen-containing functional groups at the

25 surface of the support than actually exist. Such oxygen atoms of an oxidized promoter also can interfere with obtaining a reliable prediction of noble metal leaching, noble metal sintering, and catalyst activity from the simple measurement (via, for example, x-ray photoelectron

30 spectroscopy) of oxygen atoms at the catalyst surface.

Thus, when the catalyst comprises at least one
promoter which has been exposed to an oxidant and thereby
has been oxidized (e.g., when the catalyst has been
exposed to air for more than about 1 hour), it is
5   preferred that the promoter first be substantially
reduced (thereby removing the oxygen atoms of the
oxidized promoter from the surface of the catalyst)
before attempting to measure the amount of detrimental
oxygen-containing functional groups at the surface of the
10   carbon support. This reduction preferably is achieved by
heating the catalyst to a temperature of about 500°C for
about 1 hour in an atmosphere consisting essentially of
H_2. The measurement of detrimental oxygen-containing
functional groups at the surface preferably is performed
15   (a) after this reduction, and (b) before the surface is
exposed to an oxidant following the reduction. Most
preferably, the measurement is taken immediately after
the reduction.

The preferred concentration of metal particles
20   at the surface of the carbon support depends, for
example, on the size of the metal particles, the specific
surface area of the carbon support, and the concentration
of noble metal on the catalyst. It is presently believed
that, in general, the preferred concentration of metal
25   particles is roughly from about 3 to about 1,500
particles/μm^2 (i.e., number of metal particles per μm^2 of
surface of carbon support), particularly where: (a) at
least about 80% (number density) of the metal particles
are from about 1.5 to about 7 nm in their largest
30   dimension, (b) the carbon support has a specific surface
area of from about 750 to about 2100 m^2/g (i.e., m^2 of

31

surface of carbon support per gram of carbon support),
and (c) the concentration of noble metal at the carbon
support surface is from about 1 to about 10 wt.% ([mass
of noble metal ÷ total mass of catalyst] x 100%). In

5   more preferred embodiments, narrower ranges of metal
particle concentrations and noble metal concentrations
are desired. In one such embodiment, the concentration
of metal particles is from about 15 to about 800
particles/μm^2, and the concentration of noble metal at the

10 carbon support surface is from about 2 to about 10 wt.%.
In an even more preferred embodiment, the concentration
of metal particles is from about 15 to about 600
particles/μm^2, and the concentration of noble metal at the
carbon support surface is from about 2 to about 7.5 wt.%.

15 In the most preferred embodiment, the concentration of
the metal particles is from about 15 to about 400
particles/μm^2, and the concentration of noble metal at the
carbon support surface is about 5 wt.%. The concentration
of metal particles at the surface of the carbon support

20 may be measured using methods known in the art.

B.   **Process for the Preparation of the Oxidation
      Catalyst**

1.   **Deoxygenation of the Carbon Support**

            The surface of the carbon support preferably is

25 deoxygenated before the noble metal is deposited onto it.
Preferably, the surface is deoxygenated using a high-
temperature deoxygenation treatment. Such a treatment
may be a single-step or a multi-step scheme which, in
either case, results in an overall chemical reduction of

32

oxygen-containing functional groups at the surface of the
carbon support.

In a two-step high-temperature deoxygenation
treatment, the carbon support preferably is first treated
5   with a gaseous or liquid phase oxidizing agent to convert
oxygen-containing functionalities in relatively lower
oxidation states (e.g., ketones, aldehydes, and alcohols)
into functionalities in relatively higher oxidation
states (e.g., carboxylic acids), which are easier to
10   cleave from the surface of the catalyst at high
temperatures. Representative liquid phase oxidizing
agents include nitric acid, H_2O_2, chromic acid, and
hypochlorite, with concentrated nitric acid comprising
from about 10 to about 80 grams of HNO_3 per 100 grams of
15   aqueous solution being preferred. Representative gaseous
oxidants include molecular oxygen, ozone, nitrogen
dioxide, and nitric acid vapors. Nitric acid vapors are
the preferred oxidizing agent. With a liquid oxidant,
temperatures of from about 60 to about 90°C are
20   appropriate, but with gaseous oxidants, it is often
advantageous to use temperatures from about 50 to about
500°C or even greater. The time during which the carbon
is treated with the oxidant can vary widely from about 5
minutes to about 10 hours. Preferably, the reaction time
25   is from about 30 minutes to about 6 hours. Experimental
results indicate that carbon load, temperature, oxidant
concentration, etc. in the first treatment step are not
narrowly critical to achieving the desired oxidation of
the carbon material and thus may be governed by
30   convenience over a wide range. The highest possible
carbon load is preferred for economic reasons.

33

In the second step, the oxidized carbon support is pyrolyzed (_i.e._, heated) at a temperature preferably in the range of from about 500 to about 1500°C, and more preferably from about 600 to about 1,200°C, in a

5   nitrogen, argon, helium, or other non-oxidizing environment (_i.e._, an environment consisting essentially of no oxygen) to drive off the oxygen-containing functional groups from the carbon surface. At temperatures greater than 500°C, an environment may be

10 used which comprises a small amount of ammonia (or any other chemical entity which will generate NH_3 during pyrolysis), steam, or carbon dioxide which aid in the pyrolysis. As the temperature of the carbon support is cooled to temperatures less than 500°C, however, the

15 presence of oxygen-containing gases such as steam or carbon dioxide may lead to the re-formation of surface oxides and thus, is preferably avoided. Accordingly, the pyrolysis is preferably conducted in a non-oxidizing atmosphere (_e.g._, nitrogen, argon, or helium). In one

20 embodiment, the non-oxidizing atmosphere comprises ammonia, which tends to produce a more active catalyst in a shorter time as compared to pyrolysis in the other atmospheres. The pyrolysis may be achieved, for example, using a rotary kiln, a fluidized bed reactor, or a

25 conventional furnace.

The carbon support generally is pyrolyzed for a period of from about 5 minutes to about 60 hours, preferably from about 10 minutes to about 6 hours. Shorter times are preferred because prolonged exposure of

30 the carbon at elevated temperatures tends to reduce the activity of the catalyst. Without being bound to any

34

particular theory, it is presently believed that
prolonged heating at pyrolytic temperatures favors the
formation of graphite, which is a less preferred form of
a carbon support because it normally has less surface

5   area. As discussed above, a more active catalyst
typically may be produced in a shorter time by using an
atmosphere which comprises ammonia.

In a preferred embodiment of this invention,
high-temperature deoxygenation is carried out in one

10   step. This one-step treatment may consist of merely
performing the pyrolysis step of the two-step high-
temperature deoxygenation treatment discussed above.
More preferably, however, the single-step treatment
consists of pyrolyzing the carbon support as described

15   above while simultaneously passing a gas stream
comprising N_2, NH_3 (or any other chemical entity which
will generate NH_3 during pyrolysis), and steam over the
carbon. Although it is not a critical feature of this
invention, the flow rate of the gas stream preferably is

20   fast enough to achieve adequate contact between the fresh
gas reactants and the carbon surface, yet slow enough to
prevent excess carbon weight loss and material waste. A
non-reactive gas may be used as a diluent to prevent
severe weight loss of the carbon.

25   2.   **Deposition of the Noble Metal(s)**

Methods used to deposit the noble metal onto
the surface of the carbon support are generally known in
the art, and include liquid phase methods such as
reaction deposition techniques (*e.g.*, deposition via

30   reduction of noble metal compounds, and deposition via

hydrolysis of noble metal compounds), ion exchange
techniques, excess solution impregnation, and incipient
wetness impregnation; vapor phase methods such as
physical deposition and chemical deposition;

5   precipitation; electrochemical deposition; and
electroless deposition. See generally, Cameron, D.S.,
Cooper, S.J., Dodgson, I.L., Harrison, B., and Jenkins,
J.W. "Carbons as Supports for Precious Metal Catalysts,"
Catalysis Today, 7, 113-137 (1990). Catalysts comprising

10 noble metals at the surface of a carbon support also are
commercially available, e.g., Aldrich Catalog No. 20,593-
1, 5% platinum on activated carbon (Aldrich Chemical Co.,
Inc., Milwaukee, WI); Aldrich Catalog No. 20,568-0, 5%
palladium on activated carbon.

15   Preferably, the noble metal is deposited via a
reactive deposition technique comprising contacting the
carbon support with a solution comprising a salt of the
noble metal, and then hydrolyzing the salt. An example
of a suitable platinum salt which is relatively

20 inexpensive is hexachloroplatinic acid (H_2PtCl_6). The use
of this salt to deposit platinum onto a carbon support
via hydrolytic deposition is illustrated in Example 3.
            In one embodiment of this invention, the noble
metal is deposited onto the surface of the carbon support

25 using a solution comprising a salt of a noble metal in
one of its more reduced oxidation states. For example,
instead of using a salt of Pt(IV) (e.g., H_2PtCl_6), a salt
of Pt(II) is used. In another embodiment, platinum in
its elemental state (e.g., colloidal platinum) is used.

30 Using th se more reduced metal precursors leads to less
oxidation of the carbon support and, therefore, less

oxygen-containing functional groups being formed at the
surface of the support while the noble metal is being
deposited onto the surface. One example of a Pt(II) salt
is K_2PtCl_4. Another potentially useful Pt(II) salt is

5   diamminedinitrito platinum(II). Example 11 shows that
using this salt to deposit the noble metal produces a
catalyst which is more resistant to leaching than a
catalyst prepared using H_2PtCl_6 as the metal precursor.
Without being bound by any particular theory, it is

10   believed that this is due to the fact that
diamminedinitrito platinum(II) generates ammonia in-situ
during reduction which further promotes removal of the
oxygen-containing functional groups at the surface of the
carbon support. This benefit, however, should be weighed

15   against a possible explosion danger associated with the
use of diamminedinitrito platinum(II).

3.   Deposition of the Promoter(s)

A promoter(s) may be deposited onto the surface
of the carbon support before, simultaneously with, or

20   after deposition of the noble metal onto the surface.
Methods used to deposit a promoter onto the surface of
the carbon support are generally known in the art, and
include the same methods used to deposit a noble metal
discussed above. In one embodiment, a salt solution

25   comprising the promoter is used to deposit the promoter.
A suitable salt that may be used to deposit bismuth is
$Bi(NO_3)_3 \cdot 5H_2O$, a suitable salt that may be used to deposit
iron is $FeCl_3 \cdot 6H_2O$, and a suitable salt that may be used to
deposit tin is $SnCl_2 \cdot 2H_2O$. It should be recognized that

30   more than one promoter may be deposited onto the surface

of the carbon support. Examples 13, 14, 15, and 17 demonstrate depositing a promoter onto a carbon surface with a salt solution comprising a promoter. Example 18 demonstrates depositing more than one promoter (*i.e.*, iron and Sn) onto a carbon surface using salt solutions comprising the promoters.

As noted above, a catalyst comprising a noble metal alloyed with at least one promoter is particularly preferred. There are a variety of possible preparative techniques known in the art which may be used to form a multi-metallic alloy at support surfaces. See, *e.g.*, V. Ponec & G.C. Bond, <u>Catalysis by Metals and Alloys</u>, "Studies in Surface Science and Catalysis," Vol. 95 (B. Delmon. & J.T. Yates, advisory eds., Elsevier Science B.V., Amsterdam, Netherlands).

In one of the more preferred embodiments, reactive deposition is used to form metal particles containing a noble metal alloyed with a promoter. Reactive deposition may comprise, for example, reductive deposition wherein a surface of a carbon support is contacted with a solution comprising: (a) a reducing agent; and (b) (i) a compound comprising the noble metal and a compound comprising the promoter, or (ii) a compound comprising both the noble metal and the promoter. A wide range of reducing agents may be used, such as sodium borohydride, formaldehyde, formic acid, sodium formate, hydrazine hydrochloride, hydroxylamine, and hypophosphorous acid. Compounds comprising a noble metal and/or a promoter include, for example:

1. <u>Halide compounds</u>. These include, for example, H_2PtCl_6, K_2PtCl_4, $Pt_2Br_6^{2-}$, K_2PdCl_4, $AuCl_4^{1-}$, $RuCl_3$,

$RhCl_3 \cdot 3H_2O$, K_2RuCl_6, $FeCl_3 \cdot 6H_2O$, $(SnCl_3)^{1-}$, $SnCl_4$, $ReCl_6$, $FeCl_2$, and $TiCl_4$.

2. <u>Oxide and oxy chloride compounds</u>. These include, for example, RuO_4^{2-} and M_2SnO_4.

3. <u>Nitrate compounds</u>. These include, for example, $Fe(NO_3)_3$.

4. <u>Amine complexes</u>. These include, for example, $[Pt(NH_3)_4]Cl_2$, $[Pd(NH_3)_4]Cl_2$, $Pt(NH_3)_2Cl_2$, $Pt(NH_3)_4]PtCl_4$, $Pd(NH_2CH_2CH_2NH_2)Cl_2$, $Pt(NH_2CH_2CH_2NH_2)_2Cl_2$, and $[Ru(NH_3)_5Cl]Cl_2$.

5. <u>Phosphine complexes</u>. These include, for example, $Pt(P(CH_3)_3)_2Cl_2$; $IrClCO(P(C_6H_5)_3)_2$; $PtClH(PR_3)_2$, wherein each R is independently a hydrocarbyl, such as methyl, ethyl, propyl, phenyl, etc

6. <u>Organometallic complexes</u>. These include, for example, $Pt_2(C_3H_6)_2Cl_4$; $Pd_2(C_2H_4)_2Cl_4$; $Pt(CH_3COO)_2$, $Pd(CH_3COO)_2$; $K[Sn(HCOO)_3]$; $Fe(CO)_5$; $Fe_3(CO)_{12}$; $Fe_4(CO)_{16}$; $Sn_3(CH_3)_4$; and $Ti(OR)_4$, wherein each R is independently a hydrocarbyl, such as methyl, ethyl, propyl, phenyl, etc.

7. <u>Noble metal/promoter complexes</u>. These include, for example, $Pt_3(SnCl_3)_2(C_8H_{12})_3$ and $[Pt(SnCl_3)_5]^{3-}$.

In a particularly preferred embodiment, hydrolysis reactions are used to deposit a noble metal alloyed with a promoter. In this instance, ligands containing the noble metal and promoter are formed, and then hydrolyzed to form well-mixed, metal oxide and metal hydroxide clusters at the surface of the carbon support. The ligands may be formed, for example, by contacting the surface of the support with a solution comprising (a) a

compound comprising the noble metal and a compound
comprising the promoter, or (b) a compound comprising
both the noble metal and the promoter. Suitable
compounds comprising a noble metal and/or a promoter are

5   listed above with respect to reductive deposition.
Hydrolysis of the ligands may be achieved, for example,
by heating (e.g., at a temperature of at least about
60°C) the mixture. Example 17 further demonstrates the
use of hydrolysis reactions to deposit a noble metal

10   (i.e., platinum) alloyed with a promoter (i.e., iron).

In addition to the above-described reactive
deposition techniques, there are many other techniques
which may be used to form the alloy. These include, for
example:

15   1.   Forming the alloy by introducing metal
              compounds (which may be simple or complex, and
              may be covalent or ionic) to the surface of the
              support via impregnation, adsorption from a
              solution, and/or ion exchange.

20   2.   Forming the alloy by vacuum co-deposition of
              metal vapors containing the noble metal and
              promoter onto the surface.

         3.   Forming the alloy by depositing one or metals
              onto a pre-deposited metal belonging to Group

25   8, 9, or 10 of the Periodic Table of the
              Elements (i.e., Fe, Co, Ni, Ru, Rh, Pd, Os, Ir,
              and Pt) via, for example, electrolytic or
              electroless plating.

         4.   Forming the alloy by: (a) depositing metal

30   complexes containing metals in the zero valence
              state (e.g., carbonyl, pi-allyl, or

cyclopentadienyl complexes of the noble metal
and of the promoter) at the surface of the
carbon support; and (b) removing the ligands
by, for example, heating or reduction to form

5   the alloy particles at the surface.

5.   Forming the alloy by contacting a solution
containing a metal compound (e.g., a metal
chloride or a metal alkyl compound) with a pre-
deposited metal hydride containing a metal

10   belonging to Group 8, 9, or 10 of the Periodic
Table of the Elements.

6.   Forming the alloy by co-depositing, either
simultaneously or sequentially, metal complexes
(either preformed or formed in situ) containing

15   the noble metal(s) and promoter(s) at the
surface of the carbon support.

7.   Forming the alloy by pre-forming alloy
particles as colloids or aerosols, and then
depositing the preformed alloy particles at the

20   surface of the carbon support. To illustrate,
colloidal particles containing platinum and
iron may be easily formed by boiling a dilute
solution of H_2PtCl_6 and $SnCl_2 \cdot 2H_2O$ with a sodium
citrate solution. Protecting agents (e.g.,

25   carbohydrates, polymers, lipophilic quaternary
nitrogen salts) may be used to effectively
control metal alloy particle growth. This
technique, therefore, is often useful to form a
narrow distribution of alloy particle sizes.

30   It should be recognized that the above-
discussed techniques for forming an alloy are simply

41

illustrative, and not exhaustive. Using the teachings of
this specification and the general knowledge of the art,
one of ordinary skill in the art may routinely determine
which of the numerous alloy preparation techniques known
5   in the art are suitable to a particular use.

Regardless of the technique used to form the
alloy, after the metals have been deposited at the
surface of the carbon support, it is often preferable to
dry the support using, for example, a sub-atmospheric,
10   non-oxidizing environment (preferably, N_2, a noble gas, or
both). Use of a drying step is particularly preferred
where the surface of the support is to be subsequently
reduced by heating the surface (and even more preferred
where the heating is to be conducted in a non-oxidizing
15   environment). Preferably, the support is dried to reduce
the moisture content of the support to less than about 5%
by weight.

It should be recognized that reducing the
surface of the carbon support after deposition of the
20   noble metal(s) and promoter(s) typically increases the
extent of noble metal alloyed with a promoter. Such
reduction also often tends to increase the number of
particles falling within the preferred size range.

4.   <u>Reduction of the Carbon Support Surface</u>

25   After the carbon support has been impregnated
with the noble metal(s) (and promoter(s), if any), the
surface of the catalyst preferably is reduced. The
surface of the catalyst suitably may be reduced, for
example, by heating the surface at a temperature of at
30   least about 400°C. It is especially preferable to

42

conduct this heating in a non-oxidizing environment
(e.g., nitrogen, argon, or helium). It is also more
preferred for the temperature to be greater than about
500°C. Still more preferably, the temperature is from

5   about 550 to about 1,200°C, and most preferably from
about 550 to about 900°C. Temperatures less than 400°C
tend to be unsatisfactory for removing the oxygen-
containing functional groups from the surface of the
carbon support. On the other hand, temperatures greater

10 than 1,200°C tend to reduce the activity of the catalyst.
Temperatures of from about 400 to about 500°C preferably
are used only if the surface of the carbon support has a
carbon atom to oxygen atom ratio of at least about 20:1
before the noble metal is deposited onto the surface.

15   In a particularly preferred embodiment, the
surface of the catalyst is reduced by a process
comprising exposing the surface to a reducing
environment. For example, before the heating, the
catalyst sample may be pre-treated with a liquid-phase

20 reducing agent, such as formaldehyde or formic acid.
Even more preferably, the heating is conducted in the
presence of a gas-phase reducing agent (the method of
heating the catalyst in the presence of a gas-phase
reducing agent will sometimes be referred to as "high-

25 temperature gas-phase reduction"). Various gas-phase
reducing agents may be used during the heating, including
but not limited to H_2, ammonia, and carbon monoxide.
Hydrogen gas is most preferred because the small
molecular size of hydrogen allows better penetration into

30 the deepest pores of the carbon support. Preferably, the
remainder of the gas consists essentially of a non-

43

oxidizing gas, such as nitrogen, argon, or helium. The gas may comprise any finite concentration of H_2, although H_2 concentrations of less than 1.0% are disadvantageous because of the time they tend to require to reduce the

5   surface of the support. Preferably, the gas comprises from about 5 to about 50 volume% H_2, and most preferably from about 5 to about 25 volume% H_2.

The preferred amount of time that the catalyst surface is heated depends on the mass transfer of the

10   reducing agent to the catalyst surface. When the reducing agent is a non-oxidizing gas comprising from about 10 to about 20 volume% H_2, the surface preferably is heated for from about 15 minutes to about 24 hours at from about 550 to about 900°C with a space velocity of

15   from about 1 to about 5,000 hour^{-1}. More preferably, the space velocity is from about 10 to about 2,500 hour^{-1}, and even more preferably from about 50 to about 750 hour^{-1}. In the most preferred embodiment, the heat-treatment is conducted at the above preferred temperatures and space

20   velocities for from about 1 to about 10 hours. Heating the surface at space velocities of less than 1 hour^{-1} is disadvantageous because the oxygen-containing functional groups at the surface of the carbon support may not be sufficiently destroyed. On the other hand, heating the

25   surface at space velocities greater than 5,000 hour^{-1} is uneconomical.

In accordance with this invention it has been found that pre-existing oxygen-containing functional groups at the surface of the carbon support are not

30   necessary, or even desired, to obtain adequate noble metal dispersion and retention. Without being bound by

44

any particular theory, it is believed that this heating
step enhances the platinum-carbon interaction on the
catalyst by removing oxygen-containing functional groups
at the surface of the carbon support, including those

5   formed by depositing the noble metal onto the surface.
It is believed that these oxygen-containing functional
groups are unstable anchor sites for the noble metal
because they tend to interfere with the potentially
stronger π interactions between the noble metal and the

10 carbon support. Heating alone will decompose and thereby
remove many of the oxygen-containing functional groups at
the surface of the carbon support. However, by heating
the surface in the presence of a reducing agent (e.g.,
H$_2$), more oxygen-containing functional groups are able to

15 be eliminated.

          If the carbon atom to oxygen atom ratio at the
surface of the carbon support is less than about 20:1
before the noble metal is deposited onto the surface of
the support, the surface preferably is reduced using the

20 above-described high-temperature gas-phase reduction
treatment at a temperature greater than 500°C, although
the surface may optionally be treated with other
reduction environments in addition to high-temperature
gas-phase reduction. On the other hand, if the surface

25 of the carbon support has a carbon atom to oxygen atom
ratio which is at least about 20:1 before the noble metal
is deposited onto the surface, various alternative
reduction environments may be used instead of high-
temperature gas-phase reduction.

30   The surface of the catalyst may be reduced, at
least in part, by treating it with an amine, such as

45

urea, a solution comprising ammonium ions (e.g., ammonium
formate or ammonium oxalate), or ammonia gas, with
ammonia gas or a solution comprising ammonium ions being
most preferred. This amine treatment preferably is used

5   in addition to other reduction treatments, and most
preferably is used before high-temperature gas-phase
reduction. In one such embodiment, the noble metal is
deposited onto the surface by treating it with a noble
metal precursor solution comprising ammonium ions.

10   Alternatively, after the noble metal is deposited onto
the surface of the support, the support may be washed
with a solution comprising ammonium ions or placed into
contact with a gas comprising ammonia. Most preferably,
the catalyst surface is washed with diluted aqueous

15   ammonia after depositing the noble metal. In this
instance, the catalyst is added to pure water and stirred
for a few hours to wet the surface of the catalyst.
Next, while continuing to stir the catalyst slurry, a
solution comprising ammonium ions is added to the

20   catalyst slurry in an amount sufficient to produce a pH
of greater than 7, more preferably from about 8 to about
12, and most preferably from about 9.5 to about 11.0.
Because the temperature and pressure are not critical,
this step preferably is performed at room temperature and

25   atmospheric pressure. Example 10 further demonstrates
this reduction treatment.

Sodium borohydride ($NaBH_4$) also may be used to
reduce the surface of the catalyst. As with the amine
treatment, this treatment preferably is used in addition

30   to other reduction treatments, and most preferably is
used before high-temperature gas-phase reduction.

Preferably, after depositing the noble metal onto the
surface of the support, the support is washed with a
solution of NaBH$_4$ in the presence of NaOH at a pH of from
about 8 to about 14 for about 15 to about 180 minutes.

5   The amount of NaBH$_4$ used preferably is sufficient to
reduce all the noble metal. Because the temperature and
pressure are not critical, this step preferably is
performed at room temperature and atmospheric pressure.
Example 12 further demonstrates this reduction treatment.

10   It should be recognized that any of the above
treatments which may be used to reduce the surface of the
catalyst also may be used to deoxygenate the surface of
the carbon support before the noble metal is deposited
onto the surface.

15 **C.   Use of the Oxidation Catalyst**

          The above-described catalyst may be used for
liquid phase oxidation reactions. Examples of such
reactions include the oxidation of alcohols and polyols
to form aldehydes, ketones, and acids (_e.g._, the

20 oxidation of 2-propanol to form acetone, and the
oxidation of glycerol to form glyceraldehyde,
dihydroxyacetone, or glyceric acid); the oxidation of
aldehydes to form acids (_e.g._, the oxidation of
formaldehyde to form formic acid, and the oxidation of

25 furfural to form 2-furan carboxylic acid); the oxidation
of tertiary amines to form secondary amines (_e.g._, the
oxidation of nitrilotriacetic acid ("NTA") to form
iminodiacetic acid ("IDA")); the oxidation of secondary
amines to form primary amines (_e.g._, the oxidation of IDA

30 to form glycine); and the oxidation of various acids

47

(e.g., formic acid or acetic acid) to form carbon dioxide and water.

The above-described catalyst is especially useful in liquid phase oxidation reactions at pH levels

5   less than 7, and in particular, at pH levels less than 3. It also is especially useful in the presence of solvents, reactants, intermediates, or products which solubilize noble metals. One such reaction is the oxidation of PMIDA or a salt thereof to form N-

10 (phosphonomethyl)glycine or a salt thereof in an environment having pH levels in the range of from about 1 to about 2. The description below will disclose with particularity the use of the above-described catalyst to effect the oxidative cleavage of PMIDA or a salt thereof

15 to form N-(phosphonomethyl)glycine or a salt thereof. It should be recognized, however, that the principles disclosed below are generally applicable to other liquid phase oxidative reactions, especially those at pH levels less than 7 and those involving solvents, reactants,

20 intermediates, or products which solubilize noble metals.

To begin the PMIDA oxidation reaction, it is preferable to charge the reactor with the PMIDA reagent (i.e., PMIDA or a salt thereof), catalyst, and a solvent in the presence of oxygen. The solvent is most

25 preferably water, although other solvents (e.g., glacial acetic acid) are suitable as well.

The reaction may be carried out in a wide variety of batch, semi-batch, and continuous reactor systems. The configuration of the reactor is not

30 critical. Suitable conventional reactor configurations include, for example, stirred tank reactors, fixed bed

48

reactors, trickle bed reactors, fluidized bed reactors, bubble flow reactors, plug flow reactors, and parallel flow reactors.

When conducted in a continuous reactor system, 5 the residence time in the reaction zone can vary widely depending on the specific catalyst and conditions employed. Typically, the residence time can vary over the range of from about 3 to about 120 minutes. Preferably, the residence time is from about 5 to about 10 90 minutes, and more preferably from about 5 to about 60 minutes. When conducted in a batch reactor, the reaction time typically varies over the range of from about 15 to about 120 minutes. Preferably, the reaction time is from about 20 to about 90 minutes, and more preferably from 15 about 30 to about 60 minutes.

In a broad sense, the oxidation reaction may be practiced in accordance with the present invention at a wide range of temperatures, and at pressures ranging from sub-atmospheric to super-atmospheric. Use of mild 20 conditions (e.g., room temperature and atmospheric pressure) have obvious commercial advantages in that less expensive equipment may be used. However, operating at higher temperatures and super-atmospheric pressures, while increasing plant costs, tends to improve phase 25 transfer between the liquid and gas phase and increase the PMIDA oxidation reaction rate.

Preferably, the PMIDA reaction is conducted at a temperature of from about 20 to about 180°C, more preferably from about 50 to about 140°C, and most 30 preferably from about 80 to about 110°C. At temperatures

49

greater than about 180°C, the raw materials tend to begin
to slowly decompose.

The pressure used during the PMIDA oxidation
generally depends on the temperature used. Preferably,
5   the pressure is sufficient to prevent the reaction
mixture from boiling. If an oxygen-containing gas is
used as the oxygen source, the pressure also preferably
is adequate to cause the oxygen to dissolve into the
reaction mixture at a rate sufficient such that the PMIDA
10 oxidation is not limited due to an inadequate oxygen
supply. The pressure preferably is at least equal to
atmospheric pressure. More preferably, the pressure is
from about 30 to about 500 psig, and most preferably from
about 30 to about 130 psig.

15   The catalyst concentration preferably is from
about 0.1 to about 10 wt.% ([mass of catalyst ÷ total
reaction mass] x 100%). More preferably, the catalyst
concentration preferably is from about 0.2 to about 5
wt.%, and most preferably from about 0.3 to about 1.5
20 wt.%. Concentrations greater than about 10 wt.% are
difficult to filter. On the other hand, concentrations
less than about 0.1 wt.% tend to produce unacceptably low
reaction rates.

The concentration of PMIDA reagent in the feed
25 stream is not critical. Use of a saturated solution of
PMIDA reagent in water is preferred, although for ease of
operation, the process is also operable at lesser or
greater PMIDA reagent concentrations in the feed stream.
If the catalyst is present in the reaction mixture in a
30 finely divided form, it is preferred to use a
concentration of reactants such that all reactants and

50

the N-(phosphonomethyl)glycine product remain in solution so that the catalyst can be recovered for re-use, for example, by filtration. On the other hand, greater concentrations tend to increase reactor through-put.

5   Alternatively, if the catalyst is present as a stationary phase through which the reaction medium and oxygen source are passed, it may be possible to use greater concentrations of reactants such that a portion of the N-(phosphonomethyl)glycine product precipitates.

10   It should be recognized that, relative to many commonly-practiced commercial processes, this invention allows for greater temperatures and PMIDA reagent concentrations to be used to prepare N-(phosphonomethyl)glycine while minimizing by-product

15   formation. In the commonly practiced commercial processes using a carbon-only catalyst, it is economically beneficial to minimize the formation of the NMG by-product formed by the reaction of N-(phosphonomethyl)glycine with the formaldehyde by-

20   product. With these processes and catalysts, temperatures of from about 60 to 90°C and PMIDA reagent concentrations below about 9.0 wt.% ([mass of PMIDA reagent ÷ total reaction mass] x 100%) typically are used to achieve cost effective yields and to minimize the

25   generation of waste. At these temperatures, the maximum N-(phosphonomethyl)glycine solubility typically is less than 6.5%. However, with the oxidation catalyst and reaction process of this invention, the loss of noble metal from the catalyst and catalyst deactivation have

30   been minimized and the formaldehyde is more effectively oxidized, thereby allowing for reaction temperatures as

high as 180°C or greater with PMIDA reagent solutions and slurries of the PMIDA reagent. The use of higher temperatures and reactor concentrations permits reactor throughput to be increased, reduces the amount of water

5   that must be removed before isolation of the solid N-(phosphonomethyl)glycine, and reduces the cost of manufacturing N-(phosphonomethyl)glycine. This invention thus provides economic benefits over many commonly-practiced commercial processes.

10   Normally, a PMIDA reagent concentration of up to about 50 wt.% ([mass of PMIDA reagent ÷ total reaction mass] x 100%) may be used (especially at a reaction temperature of from about 20 to about 180°C). Preferably, a PMIDA reagent concentration of up to about

15   25 wt.% is used (particularly at a reaction temperature of from about 60 to about 150°C). More preferably, a PMIDA reagent concentration of from about 12 to about 18 wt.% is used (particularly at a reaction temperature of from about 100 to about 130°C). PMIDA reagent

20   concentrations below 12 wt.% may be used, but their use is less economical because less N-(phosphonomethyl)glycine product is produced in each reactor cycle and more water must be removed and energy used per unit of N-(phosphonomethyl)glycine product

25   produced. Lower temperatures (i.e., temperatures less than 100°C) often tend to be less advantageous because the solubility of the PMIDA reagent and N-(phosphonomethyl)glycine product are both reduced at such temperatures.

30   The oxygen source for the PMIDA oxidation reaction may be any oxygen-containing gas or a liquid

comprising dissolved oxygen. Preferably, the oxygen source is an oxygen-containing gas. As used herein, an "oxygen-containing gas" is any gaseous mixture comprising molecular oxygen which optionally may comprise one or

5 more diluents which are non-reactive with the oxygen or with the reactant or product under the reaction conditions. Examples of such gases are air, pure molecular oxygen, or molecular oxygen diluted with helium, argon, nitrogen, or other non-oxidizing gases.

10 For economic reasons, the oxygen source most preferably is air or pure molecular oxygen.

The oxygen may be introduced by any conventional means into the reaction medium in a manner which maintains the dissolved oxygen concentration in the

15 reaction mixture at the desired level. If an oxygen-containing gas is used, it preferably is introduced into the reaction medium in a manner which maximizes the contact of the gas with the reaction solution. Such contact may be obtained, for example, by dispersing the

20 gas through a diffuser such as a porous frit or by stirring, shaking, or other methods known to those skilled in the art.

The oxygen feed rate preferably is such that the PMIDA oxidation reaction rate is not limited by

25 oxygen supply. If the dissolved oxygen concentration is too high, however, the catalyst surface tends to become detrimentally oxidized, which, in turn, tends to lead to more leaching and decreased formaldehyde activity (which, in turn, leads to more NMG being produced).

30 Generally, it is preferred to use an oxygen feed rate such that at least about 40% of the oxygen is

53

utilized. More preferably, the oxygen feed rate is such
that at least about 60% of the oxygen is utilized. Even
more preferably, the oxygen feed rate is such that at
least about 80% of the oxygen is utilized. Most

5   preferably, the rate is such that at least about 90% of
the oxygen is utilized. As used herein, the percentage
of oxygen utilized equals: (the total oxygen consumption
rate ÷ oxygen feed rate) x 100%. The term "total oxygen
consumption rate" means the sum of: (i) the oxygen

10 consumption rate ("R_i") of the oxidation reaction of the
PMIDA reagent to form the N-(phosphonomethyl)glycine
product and formaldehyde, (ii) the oxygen consumption
rate ("R_{ii}") of the oxidation reaction of formaldehyde to
form formic acid, and (iii) the oxygen consumption rate

15 ("R_{iii}") of the oxidation reaction of formic acid to form
carbon dioxide and water.

In one embodiment of this invention, oxygen is
fed into the reactor as described above until the bulk of
PMIDA reagent has been oxidized, and then a reduced

20 oxygen feed rate is used. This reduced feed rate
preferably is used after about 75% of the PMIDA reagent
has been consumed. More preferably, the reduced feed
rate is used after about 80% of the PMIDA reagent has
been consumed. The reduced feed rate may be achieved by

25 purging the reactor with air, preferably at a volumetric
feed rate which is no greater than the volumetric rate at
which the pure molecular oxygen was fed before the air
purge. The reduced oxygen feed rate preferably is
maintained for from about 2 to about 40 min., more

30 preferably from about 5 to about 20 min., and most
preferably from about 5 to about 15 min. While the

54

oxygen is being fed at the reduced rate, the temperature
preferably is maintained at the same temperature or at a
temperature less than the temperature at which the
reaction was conducted before the air purge. Likewise,

5   the pressure is maintained at the same or at a pressure
less than the pressure at which the reaction was
conducted before the air purge. Use of a reduced oxygen
feed rate near the end of the PMIDA reaction tends to
reduce the amount of residual formaldehyde present in the

10   reaction solution without producing detrimental amounts
of AMPA by oxidizing the N-(phosphonomethyl)glycine
product.

        Reduced losses of noble metal may be observed
with this invention if a sacrificial reducing agent is

15   maintained or introduced into the reaction solution.
Suitable reducing agents include formaldehyde, formic
acid, and acetaldehyde. Most preferably, formic acid,
formaldehyde, or mixtures thereof are used. Experiments
conducted in accordance with this invention indicate that

20   if small amounts of formic acid, formaldehyde, or a
combination thereof are added to the reaction solution,
the catalyst will preferentially effect the oxidation of
the formic acid or formaldehyde before it effects the
oxidation of the PMIDA reagent, and subsequently will be

25   more active in effecting the oxidation of formic acid and
formaldehyde during the PMIDA oxidation. Preferably from
about 0.01 to about 5.0 wt.% ([mass of formic acid,
formaldehyde, or a combination thereof ÷ total reaction
mass] x 100%) of sacrificial reducing agent is added,

30   more preferably from about 0.01 to about 3.0 wt.% of
sacrificial reducing agent is added, and most preferably

from about 0.01 to about 1.0 wt.% of sacrificial reducing agent is added.

In one preferred embodiment, unreacted formaldehyde and formic acid are recycled back into the
5   reaction mixture for use in subsequent cycles. In this instance, the recycle stream also may be used to solubilize the PMIDA reagent in the subsequent cycles.

Typically, the concentration of N-(phosphonomethyl)glycine in the product mixture may be as
10 great as 40% by weight, or greater. Preferably, the N-(phosphonomethyl)glycine concentration is from about 5 to about 40%, more preferably from about 8 to about 30%, and still more preferably from about 9 to about 15%. Concentrations of formaldehyde in the product mixture are
15 typically less than about 0.5% by weight, more preferably less than about 0.3%, and still more preferably less than about 0.15%.

Following the oxidation, the catalyst preferably is subsequently separated by filtration. The
20 N-(phosphonomethyl)glycine product may then be isolated by precipitation, for example, by evaporation of a portion of the water and cooling.

It should be recognized that the catalyst of this invention has the ability to be reused over several
25 cycles, depending on how oxidized its surface becomes with use. Even after the catalyst becomes heavily oxidized, it may be reused by being reactivated. To reactivate a catalyst having a heavily oxidized surface, the surface preferably is first washed to remove the
30 organics from the surface. It then preferably is reduced in the same manner that a catalyst is reduced after the

noble metal is deposited onto the surface of the support,
as described above.

V.   **Examples**

        The following examples are intended to further
5 illustrate and explain the process of the present
   invention.

   Example 1.   Measuring pore volume of carbon support
        A Micromeritics ASAP 2000 surface area and pore
   volume distribution instrument was used to acquire the
10 data. Total surface area determination involves exposing
   a known weight of a solid to some definite pressure of a
   non-specific adsorbate gas at a constant temperature,
   e.g., at the temperature of liquid nitrogen, -196°C.
   During equilibration, gas molecules leave the bulk gas to
15 adsorb onto the surface which causes the average number
   of molecules in the bulk gas to decrease which, in turn,
   decreases the pressure. The relative pressure at
   equilibrium, p, as a fraction of the saturation vapor
   pressure, p_o, of the gas is recorded. By combining this
20 decrease in pressure with the volumes of the vessel and
   of the sample, the amount (i.e., the number of molecules)
   of gas adsorbed may be calculated by application of the
   ideal gas laws. These data are measured at relative
   pressures (p/p_o) of approximately 0.1 to 0.3 where the
25 Brunauer, Emmett and Teller (BET) equation for multi-
   layer adsorption typically applies. With the number of
   adsorbed gas molecules known, it is possible to calculate
   the surface area using the "known" cross-sectional area
   of the adsorbate. For cases where only physical

adsorption due to Van der Waals forces occurs (<u>i.e.</u>, Type
I Langmuir isotherms) the determination of surface area
from the observed changes in pressure is accomplished
using the BET equation. Pore size and pore size

5 distributions are calculated by obtaining relative
pressure data approaching $p/p_o = 1$, <u>i.e.</u>, in the regime
where multi-layer adsorption and capillary condensation
occur. By applying the Kelvin equation and methods
developed by Barrett, Joyner and Halenda (BJH), the pore

10 volume and area may be obtained.

Example 2.   **High-temperature deoxygenation of a carbon
support**

      The high-temperature deoxygenation procedures
described in the following examples may be used with any

15 carbon support to produce a deoxygenated carbon support.

<u>Single-Step High-Temperature Deoxygenation #1 Using
NH$_3$/H$_2$O Gas</u>
      An activated carbon support (2.5 g) was placed
into a 1.9 cm I.D. x 40.6 cm length quartz tube. The

20 tube was connected to a gas stream resulting from
sparging a 70 to 100 ml/min. N$_2$ stream through a 70°C, 10%
NH$_4$OH aqueous solution. The quartz tube then was placed
into a preheated 30.5 cm tubular furnace and pyrolyzed at
930°C for 60 min. and then cooled to room temperature

25 under a dry N$_2$ atmosphere without contacting any air.

<u>Single-Step High-Temperature Deoxygenation #2 Using
NH$_3$/H$_2$O Gas</u>
      An activated carbon support (3.55 g) was placed
into a 1.9 cm I.D. x 35.6 cm long quartz tube. The tube

was connected to streams of 50 ml/min. of NH₃ gas and 89

ml/min. of steam and then placed into a preheated 30.5 cm

tubular furnace and pyrolyzed at 930°C for 30 minutes.

The tube subsequently was cooled to room temperature

5   under a dry N₂ atmosphere without any contact with air.

         To show the advantages of deoxygenating the

carbon support before dispersing the noble metal onto the

surface of the support, the performances of the following

two catalysts were compared: one having a carbon

10 support, which was deoxygenated using the above treatment

before platinum was dispersed onto its surface; and one

having an SA-30 carbon support (Westvaco Corp. Carbon,

Department Covington, VA) which was used as received from

Westvaco. Platinum was dispersed onto the surfaces of

15 the carbon supports using the technique described in

Example 3 below. The catalysts then were reduced. In

one experiment, the catalysts were reduced using NaBH₄

(See Example 12 for protocol). In a second experiment,

the catalysts were reduced by heating them in 20% H₂ and

20 80% argon for 8 hours at 640°C.

         The reduced catalysts were used to catalyze the

oxidation of PMIDA to N-(phosphonomethyl)glycine (i.e.,

"glyphosate") using the reaction conditions set forth in

Example 5. Table 1 shows the results. Use of the

25 deoxygenated carbon support resulted in smaller CO

desorption values, less noble metal leaching, higher

formaldehyde activity, and shorter reaction times.

Table 1

Effect of Deoxygenating the Carbon Support before Dispersing Noble Metal onto Its Surface

Deoxygenation treatment	CO desorption from carbon support (mmole/g)	Reduction	Pt in soln. (µg/g glyph. prod.)	CH_2O (mg/g glyph. prod.)	Reaction time[1] (min.)
Single-step high-temperature deoxygenation #2	0.23	$NaBH_4$ Reduced (Ex. 12)	8.6	28.5	35.1
SA-30, used as received	1.99	same	54.3	43.1	62.7
Single-step high-temperature deoxygenation #2	0.23	8 hrs at 640°C in 20% H2, 80% Ar	4.8	15.6	29.8
SA-30, used as received	1.99	same	31	19.7	50.7

1. When ≥98% of the PMIDA has been consumed.

60

Example 3.   **Depositing platinum onto the surface of a carbon support**

Twenty grams of NUCHAR activated carbon SA-30 (Westvaco Corp. Carbon, Department Covington, VA) was
5   slurried in 2 L of water for 2 hours. Then, 2.81 grams of H_2PtCl_6 dissolved in about 900 ml of water was added dropwise over a period of 3 to 4 hours. After the H_2PtCl_6 solution was completely added, the slurry was stirred for 90 more minutes. The pH of the slurry then was
10   readjusted to 10.5 using NaOH, and stirred for 10 to 14 more hours. The resulting slurry was filtered and washed with water until the filtrate reached a constant conductivity. The wet cake was dried at 125°C under vacuum for 10 to 24 hours. This material produced 5%
15   platinum on carbon upon reduction.

It should be recognized that the above procedure may be used to deposit platinum onto the surface of other carbon supports as well.

Example 4.   **High-temperature hydrogen reduction of a**
20   **carbon support**

Approximately 5.8 g of a dried, unreduced catalyst consisting of 5% platinum on a NUCHAR SA-30 carbon support (Westvaco Corp., Carbon Department, Covington, VA) was dehydrated <u>in-situ</u> at 135°C in argon
25   for one hour before being reduced at 640°C with 20% H_2 in argon for 11 hours. Upon cooling to room temperature under 20% H_2 in argon, the catalyst was ready to use.

It should be recognized that the above procedure may be used to heat other carbon supports as
30   well.

Example 5.   **Use of th Catalyst to Oxidize PMIDA to N-**
                    (Phosphonomethyl)glycine

This example demonstrates the use of high-
temperature gas-phase reduction to improve catalyst
5 performance.

An Aldrich catalyst consisting of 5% platinum
on an activated carbon support (catalog No. 20,593-1,
Aldrich Chemical Co., Inc., Milwaukee, WI) was heated at
640°C for 4-6 hours in the presence of 20% H_2 and 80%
10 argon. Subsequently, it was used to catalyze the
oxidation of PMIDA to Glyphosate. Its performance was
compared to the performance of a sample of the Aldrich
catalyst which was used as received from Aldrich.

The PMIDA oxidation reaction was conducted in a
15 200 ml glass reactor using 11.48 g of PMIDA, 0.5%
catalyst (dry basis), a total reaction mass of 140 g, a
temperature of 90°C, a pressure of 50 psig, a stir rate
of 900 rpm, and an oxygen flow rate of 100 ml/min.

Table 2 shows the results. The high-
20 temperature hydrogen-reduced catalyst had less leaching,
better formaldehyde activity, and produced less NMG.
Also, reaction time was shortened by 30% when the high-
temperature hydrogen-reduced catalyst was used.

Table 2

PMIDA Oxidation

Results for 5% Pt on Activated Carbon (Aldrich Cat. No. 20,593-1)

Catalyst	As Received	High-Temp., H_2 Reduced
PMIDA (%)	0.4619	0.4430
N-(phosphonomethyl)glycine (%)	5.58	5.54
HCO_2H (mg/g glyph. prod.)	46.99	35.87
CH_2O (mg/g glyph. prod.)	32.96	14.60
NMG (mg/g glyph. prod.)	3.58	1.32
AMPA (ppm)	172.5	182.0
End Point (min.)	64.67	44.17
Pt in soln. (μg/g glyph. prod.)	32.26	10.50
% of Pt Lost	0.72	0.232

Example 6.   Further Examples Showing Use of Catalyst to Oxidize PMIDA to N-(Phosphonomethyl)glycine

This example demonstrates using the high-temperature, gas-phase reduction treatment and ammonia washing to improve catalyst performance.

The performances of six catalysts in catalyzing the PMIDA oxidation were compared. These catalysts were: (a) a catalyst consisting of 5% platinum on an activated carbon support (Catalog No. 33,015-9, Aldrich Chemical Co., Inc., Milwaukee, WI); (b) the catalyst after being washed with ammonia (ammonia washing was conducted using the same technique described in Example 10 except that the pH of the catalyst slurry was adjusted to and maintained at 11.0 rather than 9.5); (c) the catalyst after being heated at 75°C in 20% H_2 and 80% argon for 4-6 hours (GPR@75°C); (d) the catalyst after being heated at 640°C for 4-6 hours in the presence of 20% H_2 and 80% argon (GPR@640°C); and (e) two catalysts after being washed with ammonia and then heated at 640°C for 4-6 hours in the presence of 20% H_2 and 80% argon. The PMIDA oxidation reaction conditions were the same as in Example 5.

Table 3 shows the results. The untreated catalyst showed relatively high leaching and poor formaldehyde activity. High-temperature gas-phase reduction at 640°C in the presence of H_2 leads to the greatest decrease in leaching and increase in formaldehyde activity. Heating the catalyst at 75°C in 20% H_2 at 75°C decreased leaching to a lesser extent, but did not enhance the formaldehyde activity.

64

Table 3

PMIDA Oxidation Results for 5% Pt on Activated Carbon (Aldrich Cat. No. 33,015-9)

Catalyst	As-received	NH₃ wash w/o GPR[1]	GPR@75°C	GPR@640°C	NH₃ wash + GPR@640°C	NH₃ wash + GPR@640°C
PMIDA (%)	ND	ND	ND	0.097	0.083	ND
Glyphosate (%)	5.87	5.65	5.81	5.89	5.85	5.91
HCO_2H (mg/g glyph. prod.)	43.46	43.65	38.97	42.14	46.91	52.12
CH_2O (mg/g glyph. prod.)	19.39	22.73	19.85	13.78	15.70	17.61
NMG (mg/g glyph. prod.)	1.27	0.89	0.89	1.00	1.31	1.68
AMPA (ppm)	149.4	147.6	134.6	349.8	324.8	283.8
End Point (min.)	39.33	44.33	38	31.42	34.33	33.33
Pt in soln. (μg/g glyph. prod.)	42.59	40.71	27.54	5.26	5.30	4.23
% of Pt Lost	1	0.92	0.64	0.12	0.12	0.1

1. "GPR" means reduction in H_2
2. "ND" means none detected.

In the next experiment, five catalysts were analyzed while catalyzing the PMIDA oxidation. These catalysts were: (a) a catalyst consisting of 5% platinum on NUCHAR SA-30 (Westvaco Corp., Carbon Department,

5 Covington, VA); (b) the catalyst after being treated with NaBH$_4$ (see Example 12 for protocol); (c) the catalyst after being heated at 75°C in 20% H$_2$ and 80% argon for 4-6 hours (GPR@75°C); (d) the catalyst after being heated at 640°C in 20% H$_2$ and 80% argon for 4-6 hours (GPR@640°C);

10 (e) the catalyst after being washed with ammonia (using the same technique described in Example 10) and then heated at 640°C in 20% H$_2$ and 80% argon for 4-6 hours. The reaction conditions were the same as those in Example 5.

15   Table 4 shows the results. The untreated catalyst showed relatively high platinum leaching and low formaldehyde activity. The catalyst also showed high leaching and low formaldehyde activity after being treated with NaBH$_4$, as did GPR@75°C. In contrast,

20 GPR@640°C showed a greater formaldehyde activity and less leaching.

Table 4

PMIDA Oxidation Results Using 5% Pt on NUCHAR SA-30

Catalyst	Unreduced	NaBH$_4$ red.	GPR@75°C	GPR@640°C	NH$_3$ wash + GPR@640°C
Glyphosate (%)	2.50	5.71	4.92	5.17	5.19
HCO$_2$H (mg/g glyph. prod.)	59.56	51.14	57.85	30.85	38.21
CH$_2$O (mg/g glyph. prod.)	115.28	43.13	48.52	19.67	20.79
NMG (mg/g glyph. prod.)	1.64	2.17	6.41	0.37	1.73
AMPA (ppm)	58.16	193.9	174.0	138.5	156.3
End point (min.)	62.67	62.67	70.67	50.67	59.33
Pt in soln. (μg/g glyph. prod.)	84.00	54.29	81.30	30.95	19.27
% of Pt Lost	0.84	1.24	1.6	0.64	0.4

Example 7.   **Effect of C/O and O/Pt ratios at the surface of the catalyst**

The carbon atom to oxygen atom ratio and the oxygen atom to platinum atom ratio at the surfaces of various fresh catalysts were analyzed using a PHI Quantum 2000 ESCA Microprobe Spectrometer (Physical Electronics, Eden Prairie, MN). The surface analysis was performed by electron spectroscopy for chemical analysis ("ESCA") with the instrument in a retardation mode with the analyzer at fixed band pass energy (constant resolution). The analysis entails irradiation of the sample with soft X-rays, e.g., Al K_α (1486.6 eV), whose energy is sufficient to ionize core and valence electrons. The ejected electrons leave the sample with a kinetic energy that equals the difference between the exciting radiation and the "binding energy" of the electron (ignoring work function effects). Because only the elastic electrons, i.e., those that have not undergone energy loss by any inelastic event, are measured in the photoelectron peak, and because the inelastic mean free path of electrons in solids is short, ESCA is inherently a surface sensitive technique. The kinetic energy of the electrons is measured using an electrostatic analyzer and the number of electrons are determined using an electron multiplier. The data are presented as the number of electrons detected versus the binding energy of the electrons. ESCA survey spectra were taken using monochromatic Al K_α x-rays for excitation of the photoelectrons with the analyzer set for a 117 eV band pass energy. The X-ray source was operated at 40 watts power and data were collected from the 200 μm spot on the sample being

68

irradiated. These conditions give high sensitivity but low energy resolution. The spectra were accumulated taking a 1.0 eV step size across the region from 1100 eV to 0 eV and co-adding repetitive scans to achieve

5 acceptable signal/noise in the data. The elements present were identified and quantified using the standard data processing and analysis procedures provided with the instrumentation by the vendor. From the relative intensities of the photoelectron peaks, the relative

10 atomic concentrations of the elements Pt/C/O are obtained. ESCA analysis is generally cited as having a precision of ±20% using tabulated response factors for a particular instrument configuration.

Table 5 shows the C/O and O/Pt ratios at the
15 surface of each fresh catalyst, and the amount of leaching for each of the catalysts during a single-cycle PMIDA oxidation reaction.

Table 5
Effects of C/O and O/Pt Ratios During PMIDA Oxidation[1]

Catalyst	Reduction Treatment After Noble Metal Depo.	C/O Ratio	O/Pt Ratio	Pt in Soln. ($\mu g/g$)[2]	CH_2O (mg/g)[3]
5% Pt on deoxygenated carbon[5]	$NaBH_4$ Reduced	23.7	3	ND[4]	
same	Pt(II)[6] 640°C/9hr/10%H_2	35.3	17	1.2	24.44
same	$NaBH_4$ Reduced	21.1	3	6.9	
Aldrich Cat. No. 33015-9	640°C/6hr/20%H_2	67.9	3	5.2	13.78
same	75°C/6hr/20%H_2	13.4	10	27.5	19.85
same	Used as Received	13.3	10	42.6	19.39
Aldrich Cat. #20593-1	640°C/6hr/20%H_2 NH_3 wash/pH=11	45.2	7	10.5	21.90
same	640°C/6hr/20%H_2	37.7	10	10.5	14.60
same	Used as Received	9.1	26	32.3	32.96
5% Pt on SA-30 Westvaco carbon	640°C/7hr/20%H_2 NH_3 wash/pH=9.5	67.7	8	19.3	20.79
same	640°C/8hr/20%H_2	63.3	8	30.9	19.67
same	75°C/7hr/20%H_2	13.2	32	81.3	48.52

1. The reaction conditions were the same as those used in Example 5.

70

2.   μg Pt which leached into solution per gram
      Glyphosate produced.

3.   mg formaldehyde per gram Glyphosate produced.

4.   "ND" means none detected.

5.   5.   The carbon support was deoxygenated using the singe-
            step high-temperature deoxygenation technique #2
            described in Example 2.

6.   The Pt was deposited using diamminedinitrito P(II)
      as described in Example 11.

10   **Example 8.   Analysis of catalyst surface using
                         thermogravimetric analysis with in-line
                         mass spectroscopy (TGA-MS)**

          The concentration of oxygen-containing

     functional groups at the surfaces of various fresh

15   catalysts was determined by thermogravimetric analysis

     with in-line mass spectroscopy (TGA-MS) under helium. To

     perform this analysis, a dried sample (100 mg) of fresh

     catalyst is placed into a ceramic cup on a Mettler

     balance. The atmosphere surrounding the sample then is

20   purged with helium using a flow rate 150 ml/min. at room

     temperature for 10 minutes. The temperature subsequently

     is raised at 10°C per minute from 20 to 900°C, and then

     held at 900°C for 30 minutes. The desorptions of carbon

     monoxide and carbon dioxide are measured by an in-line

25   mass spectrometer. The mass spectrometer is calibrated

     in a separate experiment using a sample of calcium

     oxalate monohydrate under the same conditions.

          Table 6 shows the amount of carbon monoxide

     desorbed per gram of each catalyst using TGA-MS, and the

30   amount of leaching for each of the catalysts during a

single-cycle PMIDA oxidation reaction using the same
reaction conditions as in Example 5. As Table 6 shows,
leaching tends to decrease as the amount of CO desorption
decreases, and is particularly low when the desorption is
5 no greater than 1.2 mmole/g (mmole CO desorbed per gram
of catalyst).

Table 6
Effects of Oxygen-Containing Functional Groups
Which Desorb from Catalyst Surface as CO during TGA-MS

Catalyst	Reduction Treatment	TGA-MS (mmole/g)[1]	Pt in Soln. (μg/g)[2]	CH_2O (mg/g)[3]
Aldrich Cat. #33015-9	640°C/6hr/20%H_2	0.41	5.2	13.78
same	640°C/6hr/20%H_2 NH_3 wash/pH=9.5	0.38	5.3	15.70
same	75°C/6hr/20%H_2	1.87	27.5	19.85
same	NH_3 wash/pH=9.5	1.59	40.7	22.73
same	Used as Received	1.84	42.6	19.39

20 1.   mmole of CO per gram of catalyst

2. μg of noble metal which leaches into solution per
      gram of Glyphosate produced

3.   mg of formaldehyde per gram of Glyphosate produced

Example 9.   Effect of temperature during high-
                  temperature gas-phase reduction

        This example demonstrates the effects of using
various temperatures when heating the catalyst in the
5   presence of a reducing agent.

        An unreduced catalyst having 5% platinum on an
activated carbon support (which was deoxygenated using
the single-step high-temperature deoxygenation technique
#2 described in Example 2 before the platinum is
10 deposited) was heated at various temperatures in 10% H_2
and 90% argon for about 2 hours. The catalyst then was
used to catalyze the PMIDA oxidation reaction. The
reaction was conducted in a 250 ml glass reactor using 5
g PMIDA, 0.157% catalyst (dry basis), 200 g total
15 reaction mass, a temperature of 80°C, a pressure of 0
psig, and an oxygen flow rate of 150 ml/min.

        The results are shown in Table 7. Increasing
the reduction temperature from 125°C to 600°C reduces the
amount of noble metal leaching and increases the
20 formaldehyde oxidation activity during the oxidation
reaction of PMIDA into Glyphosate.

Table 7
Effects of Reduction Temperature

Reduction Temperature (°C)	Pt in Soln. (normalized[1])	CH$_2$O (normalized[2])	C/O Ratio	O/Pt Ratio
125	1.00	0.41	26	13
200	0.44	0.80	27	14
400	0.18	0.93	42	10
500	0.14	0.95	32	14
600	0.06	1.00	40	11

1. A normalized value of 1.00 corresponds to the highest amount of Pt observed in solution during this experiment.

2. A normalized value of 1.00 corresponds to the highest formaldehyde activity during this experiment.

Example 10.   Washing the catalyst with ammonia

An unreduced catalyst (6.22 g) consisting of 5% platinum on an activated carbon support (which was deoxygenated using the single-step high-temperature deoxygenation technique #2 described in Example 2 before the platinum was deposited onto the support) was slurried in 500 ml of water for 30 minutes. Afterward, the pH of the slurry was adjusted to 9.5 with diluted aqueous ammonia, and the slurry was stirred for one hour, with aqueous ammonia being periodically added to maintain the pH at 9.5. The resulting slurry was filtered and washed once with about 300 ml of water. The wet cake then was dried at 125°C under vacuum for about 12 hours. This catalyst was heated at 640°C for 11 hours in 10% H$_2$ and 90% argon, and then compared with two other catalysts consisting of 5% platinum on NUCHAR activated carbon:

(a) one reduced at room temperature with NaBH$_4$ (<u>see</u>
Example 12 for protocol), and (b) one heated at 640°C in
10% H$_2$ and 90% argon for 11 hours. The reactions were the
same as those in Example 5.

5   The results are shown in Table 8. Platinum
leaching was the lowest with the catalyst which was
washed with ammonia before high-temperature hydrogen
reduction.

Table 8
<u>Effects of Ammonia Washing</u>

Catalyst	CH$_2$O (mg/g)[1]	HCO$_2$H (mg/g)	NMG (mg/g)	Pt in soln. (μg/g)
NH$_3$-washed, High-Temp., H$_2$-reduced	10.62	28.79	0.83	0.50
High-temp., H$_2$-reduced	14.97	27.82	1.38	4.64
Room-Temp., NaBH$_4$-reduced	28.51	70.16	2.59	8.64

1. These quantities are per gram Glyphosate produced.

**Example 11.   Use of a less oxidizing noble metal
                precursor**

Platinum was deposited on an activated carbon
25 support using diamminedinitrito platinum (II).
Approximately 20 g of an activated carbon support was
deoxygenated using the single-step high-temperature
deoxygenation technique #2 described in Example 2. Next,
it was slurried in 2 L of water for 2 hours.

75

Approximately 51.3 g of a 3.4% solution of

diamminedinitrito platinum (II), diluted to 400 g with

water, then was added dropwise over a period of 3-4

hours. After addition was complete, stirring was

5   continued for 90 more minutes. The pH was re-adjusted to

10.5 by adding diluted aqueous NaOH, and stirring was

conducted for 10-14 more hours. The slurry then was

filtered and washed with a plentiful amount of water

until the filtrate reached constant conductivity. The

10   wet cake was dried at 125°C under vacuum for 10-24 hours.

The resulting catalyst was heated at 640°C for 4-6 hours

in 10% H_2 and 90% argon.

A control was prepared using H_2PtCl_6 to deposit

platinum onto the same carbon. The control was heated

15   under the same conditions as the catalyst prepared using

diamminedinitrito platinum (II).

These catalysts were compared while catalyzing

the PMIDA oxidation reaction. The reaction conditions

were the same as those in Example 5.

20   The catalyst prepared using diamminedinitrito

platinum (II) showed less leaching than the control.

Only 1.21 μg platinum per gram of Glyphosate produced

leached into solution, which was about three times better

than the control.

25   **Example 12.   Reducing the catalyst surface using NaBH₄**

The purpose of this example is to demonstrate

the effects of reducing the catalyst using NaBH₄.

Approximately 5 g of an activated carbon

support (which was deoxygenated using the single-step

high-temperature deoxygenation technique #2 described in
Example 2 before the platinum was deposited onto the
support) was slurried with 85 ml of distilled water in a
250 ml round bottom flask. The slurry was stirred in a
5   vacuum for about 1 hour. Next, 0.706 g of H_2PtCl_6 in 28
ml of distilled water was added to the slurry at a rate
of about 1 ml per 100 seconds with the vacuum still being
applied. After stirring overnight in the vacuum, the
reactor was brought to atmospheric pressure by admitting
10 a flow of N_2. After allowing the slurry to settle,
approximately 30 ml of colorless supernatant was
decanted. The remaining slurry was transferred to a 100
ml Teflon round bottom. At this point, the pH was
adjusted to 12.2 with 0.3 g of NaOH. Then, 2.3 ml of
15 $NaBH_4$ in 14 M NaOH was added at 0.075 ml/min.
Subsequently, the resulting slurry was stirred for one
hour, filtered, and washed five times with 50 ml of
distilled water. The catalyst then was dried at 125°C
and 6 mmHg for 12 hours.

20   The resulting catalyst was used to catalyze the
PMIDA oxidation. The reaction was conducted in a 300 ml
stainless steel reactor using 0.5% catalyst, 8.2% PMIDA,
a total reaction mass of 180 g, a pressure of 65 psig, a
temperature of 90°C, an agitation rate of 900 rpm, and an
25 oxygen feed rate of 72 ml/min.

            A control experiment also was conducted at the
same reaction conditions using 5.23% platinum on an
activated carbon support (which was deoxygenated using
the single-step high-temperature deoxygenation technique
30 #2 described in Example 2 before the platinum was
deposited onto the support)..

77

Table 9 shows the results using the NaBH₄-
reduced catalyst, and Table 10 shows the results of the
control experiment. Reducing with NaBH₄ reduced the
amount of noble metal leaching. It also reduced the

5 amount of formaldehyde and NMG after a period of use.

Table 9
Results Using Catalyst Treated with NaBH₄

Run #	1	2	3	4	5	6
Glyphosate (%)	5.79	5.81	5.75	5.74	5.79	5.77
PMIDA (%)	0.23	0.08	0.13	0.22	0.13	0.13
CH₂O (mg/g glyph)	28.5	31.5	47.8	38.8	41.6	45.8
HCO₂H (mg/g glyph)	70.2	90.5	100.5	96.6	98.8	99.0
AMPA/MAMPA (%)	0.02	0.01	0.01	0.01	0.01	0.01
NMG (mg/g glyph)	2.6	3.6	3.6	4.2	4.7	4.7
Pt in Soln. (μg/g glyph.)	8.64	8.60	5.22	6.96	6.91	5.20
% of Pt Lost	0.20	0.20	0.12	0.16	0.16	0.12

Table 10
Results Using Catalyst which was not treated with NaBH₄

Run #	1	2	3	4	5	6
Glyphosate (%)	5.36	5.63	5.37	5.50	5.56	5.59
PMIDA (%)	0.18	0.15	0.25	0.21	0.18	0.23
CH₂O (%)	20.9	23.6	38.4	44.2	47.7	58.3
HCO₂H (%)	27.8	63.8	96.5	98.4	102.2	102.0
AMPA/MAMPA (%)	0.04	0.02	0.04	0.02	0.02	0.03
NMG (mg/g glyph)	1.5	3.0	5.4	6.9	10.6	7.3
Pt in Soln (μg/g glyph.)	63.6	62.2	44.7	34.6	28.8	28.6
% of Pt Lost	1.30	1.34	0.92	0.73	0.61	0.61

30 **Example 13.   Use of bismuth as a promoter**

A 500 g solution was prepared consisting of 10^{-3}
M Bi(NO₃)₃·5H₂O in 10^{-3} M formic acid solution. This
solution was added to 500 g of a 5% formaldehyde solution

containing 6.0 g of 5% platinum on an activated carbon
support. The solution was stirred at 40°C under N_2
overnight and then filtered with a Buchner funnel. An
aliquot was dried and subsequently analyzed by X-ray

5   fluorescence. The catalyst had a loss on drying ("LOD")
of 63%. The dry catalyst was found to contain
approximately 3% bismuth and 4% platinum.

The following were placed into a 300 ml
stainless steel autoclave: 16.4 g of PMIDA; 4.16 g of an

10   activated carbon catalyst, 0.68 g of the above catalyst
consisting of 3% bismuth /4% platinum on its surface, and
179.4 g of water. The reaction was conducted at a
pressure of 65 psig, a temperature of 90°C, an oxygen
flow rate of 38 ml/min., and a stir rate of 900 rpm. The

15   reaction was allowed to proceed until the PMIDA was
depleted. The Glyphosate solution was separated from the
catalyst via filtration and the solution was neutralized
with 6 g of 50% NaOH solution. The catalyst was recycled
with no purge through 5 runs. Analysis of the Glyphosate

20   solution was done for each run. Two controls also were
conducted in the same manner as above except that the
0.68 g of the Bi/Pt/carbon catalyst was omitted.

The results are shown in Table 11. The runs
having the Bi/Pt/carbon catalyst produced lower levels of

25   formaldehyde, formic acid, and NMG in the product.

Table 11

PMIDA Oxidation Results Using Pt/Bi/C Catalyst

	CONTROL #1	CONTROL #2	1ST RUN	2ND RUN	3RD RUN	4TH RUN	5TH RUN
Glyphosate (%)	5.7	5.59	5.69	5.72	5.87	5.74	5.68
PMIDA (%)	ND	ND	0.04	0.07	0.085	0.04	0.046
AMPA (%)	0.034	0.031	0.015	0.009	0.008	DBNQ[1]	DBNQ
CH_2O (mg/g glyph. prod.)	142	138	28	31	34	38	42
HCO_2H (mg/g glyph. prod.)	56	57	DBNQ	7	14	17	23
AMPA/MAMPA (%)	0.047	0.041	0.021	0.014	0.013	0.014	0.013
NMG (mg/g glyph. prod.)	16.3	19.3	0.7	0.9	1.4	2.3	2.6

1. DBNQ = detectable, but not quantitated.

Example 14.   **Depositing a Tin Promoter on a Carbon Support**

An activated carbon (20 g) was slurried in about 2 L of water. Next, 0.39 g of $SnCl_2 \cdot 2H_2O$ was

5   dissolved in 500 g of 0.5% HNO_3. The solution was added dropwise to the carbon slurry. After all the solution was added, the slurry was stirred for 2 hours. The pH then was adjusted to 9.5, and the slurry was stirred for a few more hours. Next, the slurry was filtered and

10   washed with a plentiful amount of water until the filtrate reached a constant conductivity. The wet cake was dried at 125°C under vacuum to give 1% tin on carbon. Following drying, the 1% tin on carbon was calcined in argon at 500°C for 6 hours.

15   To deposit platinum onto the carbon support, 5 g of the 1% tin on carbon first was slurried in about 500 ml of water. Then 0.705 g of H_2PtCl_6 was dissolved in about 125 ml of water and added dropwise. After all the H_2PtCl_6 solution was added, the slurry was stirred for 2.5

20   hours. The pH then was adjusted to 9.5 with diluted NaOH and stirring was continued for a few more hours. The slurry then was filtered and washed with a plentiful amount of water until the filtrate reached constant conductivity. The wet cake was dried at 125°C under

25   vacuum.

This technique produced a catalyst comprising 5% platinum and 1% tin on carbon.

Example 15.   Depositing an Ir n Promoter onto a Carbon
Support

Approximately 5 g of activated carbon was
slurried in about 500 ml of water. Next, 0.25 g of
5 $FeCl_3 \cdot 6H_2O$ was dissolved in 75 ml of water. The solution
was added dropwise to the carbon slurry. After all the
solution was added, the slurry was stirred for two hours.
The slurry then was filtered and washed with a plentiful
amount of water until the filtrate reached a constant
10 conductivity. The wet cake was dried at 125°C under
vacuum to give 1% iron on carbon. Following drying, the
1% iron on carbon was calcined in argon at about 500°C
for 8 hours.

To deposit platinum onto the surface of the
15 carbon support, 2.5 g of the 1% iron on carbon first was
slurried in about 180 ml of water. Then, 0.355 g of
H_2PtCl_6 was dissolved in about 70 ml of water and added
dropwise. After all the solution was added, the slurry
was stirred for three more hours. The pH then was
20 adjusted to about 10.0 with diluted NaOH and stirring was
continued for a few more hours. Next, the slurry was
filtered and washed with a plentiful amount of water
until the filtrate reached a constant conductivity. The
wet cake was dried at 125°C under vacuum.
25   This technique produces a catalyst comprising
5% platinum and 1% iron on carbon.

Example 16.   Effect of Presence of Noble Metal on the
Surface of the Carbon Support

This example shows the advantages of using a
30 carbon support having a noble metal on its surface for

82

effecting the oxidation of PMIDA rather than a carbon-only catalyst having no noble metal on its surface.

The PMIDA oxidation reaction was conducted in the presence of a carbon-only catalyst which was
5 deoxygenated using the single-step high-temperature deoxygenation technique #2 described in Example 2. The reaction was carried out in a 300 ml stainless steel reactor using 0.365% catalyst, 8.2% PMIDA, a total reaction mass of 200 g, a pressure of 65 psig, a
10 temperature of 90°C, an agitation rate of 900 rpm, and an oxygen feed rate of 38 ml/min.

Table 12 shows the reaction times (i.e., the time for at least 98% of the PMIDA to be consumed) of 5 cycles for the carbon-only catalyst. Table 12 also shows
15 the reaction times for the two Pt-on-carbon catalysts in Example 12 over 6 cycles under the reaction conditions described Example 12. As may be seen from Table 12, the deactivation of the carbon-only catalyst per cycle generally tends to be greater (i.e., the reaction times
20 tend to increase more per cycle) than the deactivation of the carbon catalysts which had a noble metal on their surfaces. The deactivation particularly appears to be less where the catalyst has been reduced with NaBH$_4$ after the noble metal was deposited onto the surface. Without
25 being bound by any particular theory, it is believed that the deactivation of the catalyst reduced with NaBH$_4$ was less than the deactivation of the other Pt-on-carbon catalyst because the platinum on the NaBH$_4$ catalyst leached less than the platinum on the other Pt-on-carbon
30 catalyst. See Example 12, Tables 9 & 10.

Table 12
Results Using Catalyst which was not treated with NaBH₄

Run #	1	2	3	4	5	6
Run Time for Carbon-Only Catalyst (min.)	45.4	55.0	64.4	69.8	75.0	
Run Time for 5% platinum on Carbon Catalyst which was Reduced with NaBH₄ (min.)	35.1	NA[1]	NA	35.2	35.8	35.8
Run Time for 5.23% platinum on Carbon Catalyst (min.)	40.4	42.0	44.2	44.1	44.9	52.7

1.   Not available due to temperature problems.

Example 17.   The Effect of Using a Catalyst Comprising a Noble Metal Alloyed with a Promoter

This example shows the advantages of a catalyst comprising platinum alloyed with iron.

1.   **Catalyst comprising platinum alloyed with iron**

To prepare the catalyst comprising platinum alloyed with iron, approximately 10 grams of an activated carbon was slurried in about 180 ml of water. Next, 0.27 grams of $FeCl_3 \cdot 6H_2O$ and 1.39 grams of H_2PtCl_6 hydrate were co-dissolved in about 60 ml of water. This solution was added dropwise to the carbon slurry over a period of about 30 minutes. During the addition, the pH of the slurry dropped and was maintained at from about 4.4 to about 4.8 using a dilute NaOH solution (i.e., a 1.0 to 2.5 molar solution of NaOH). Afterward, the slurry was

stirred for 30 more minutes. at a pH of about 4.7. The
slurry then was heated under N₂ to 70°C at a rate of about
2°C/min. while maintaining the pH at about 4.7. Upon
reaching 70°C, the pH was raised slowly over a period of
5   about 30 minutes to 6.0 with addition of the dilute NaOH
solution. The stirring was continued for a period of
about 10 min. until the pH became steady at about 6.0.
The slurry was then cooled under N₂ to about 35°C.
Subsequently, the slurry was filtered, and the cake was
10   washed with approximately 800 ml of water 3 times. The
cake was then dried at 125°C under a vacuum. This
produced a catalyst containing 5 wt.% platinum and 0.5
wt.% iron on carbon upon heating at 690°C in 20% H₂ and
80% Ar for 1-6 hr.

15   This catalyst was analyzed via electron
microscopy, as described in more detail in Example 19.
Figure 1 is an image obtained through TEM of the carbon
support. This image shows that the alloyed metal
particles were highly dispersed and uniformly distributed
20   throughout the carbon support (the white dots represent
the metal particles; and the variations in the background
intensity are believed to represent the change of the
local density of the porous carbon). The average size of
the particles was about 3.5 nm, and the average distance
25   between particles was about 20 nm. **Figure 2** is a typical
high energy resolution X-ray spectra from an individual
metal particle of the catalyst. As **Figure 2** shows, both
platinum and iron peaks were present (the copper peaks
originated from the scattering of the copper grids).
30   Quantitative analysis of the high energy resolution X-ray
spectra from different individual metal particles showed

that the composition of the particles, within
experimental error, did not vary with the size or the
location of the metal particles on the catalyst surface.

2.   **Catalyst in which platinum was less alloyed with**
5   **iron**

To prepare the Pt/Fe/C catalyst in which the
platinum was less alloyed with iron (i.e., this catalyst
has less platinum alloyed with iron than does the first
catalyst described in this example), the platinum and
10   iron were deposited sequentially onto the surface of the
carbon support. Approximately 5 grams of an activated
carbon was slurried in about 500 ml of water. The pH was
adjusted to about 5.0 with 1N HCl. Next, about 0.25
grams of $FeCl_3 \cdot 6H_2O$ was dissolved in 75 ml of water. This
15   solution was added dropwise to the carbon slurry over a
period of about 60 min. After all the solution was
added, the slurry was stirred for about 2 hours. The pH
was adjusted to 9.5 with the dilute NaOH solution, and
the slurry was stirred for a few more hours. Afterward,
20   the slurry was filtered and washed with a plentiful
amount of water. The wet cake was dried at 125°C under
vacuum to produce 1 wt.% iron on carbon. Following
drying, this 1 wt.% iron on carbon was reduced with an
atmosphere containing 20% H_2 and 80% Ar at 635°C for 1-6
25   hr. About 2.5 grams of this 1 wt.% iron on carbon was
slurried in 250 ml of water. Next, about 0.36 grams of
H_2PtCl_6 hydrate was dissolved in 65 ml of water, which, in
turn, was added dropwise to the slurry over a period of
about 60 min. After all the solution was added, the
30   slurry was stirred for 2 hours. The slurry then was

filtered and washed with a plentiful amount of water.
The cake was then re-slurried in 450 ml of water. After
adjusting the pH of the slurry to 9.5 with the dilute
NaOH solution, the slurry was stirred for about 45 min.

5   Next, the slurry was filtered and washed once with 450 ml
of water. The wet cake was the dried at 125°C under
vacuum. This produced a catalyst containing 5 wt.%
platinum and 1 wt.% iron on carbon upon reduction by
heating to a temperature of 660°C in an atmosphere

10 containing 20% H_2 and 80% Ar for 1-6 hr.

3. Comparison of the two catalysts

These two catalysts were compared while
catalyzing the PMIDA oxidation reaction. The reaction
conditions were the same as those in Example 5. Table 13

15 shows the results. The first catalyst described in this
example (i.e., the catalyst comprising a greater amount
of platinum alloyed with iron) had greater stability with
respect to CH_2O & HCO_2H activities; the second catalyst
described in this example (i.e., the catalyst comprising

20 a lower amount of platinum alloyed with iron) deactivated
rapidly. In addition, the first catalyst retained almost
half of its iron content over 25 cycles, while the second
catalyst lost most of its iron in the first cycle.

Table 13

Comparison of Catalyst Having Pt/Fe Alloy with Catalyst Having Less Pt/Fe Alloy

Alloyed Pt & Fe	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	cycle 7	cycle 8	cycle 9	cycle 10	cycle 11	cycle 12	cycle 13
CH$_2$O (mg/g glyph. prod.)	10.49	10.7	9.23		6.04		4.92		4.44		5.08		5.24
HCO$_2$H (mg/g glyph. prod.)	19.91		29.64		27.84		25.62		27.99		29.73		28.95
NMG (mg/g glyph. prod.)	0.22		0.44		0.28		0		0		0		0
Pt in soln. (µg/g glyph. prod.)	5.08		4.87		3.6		3.06						
% of Fe Lost	44		1.9		1.2		0.8						

Less alloyed Pt & Fe	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	cycle 7	cycle 8	cycle 9	cycle 10	cycle 11	cycle 12	cycle 13
CH$_2$O (mg/g glyph. prod.)	10.16	10.7	12.24	13.56	14.68								
HCO$_2$H (mg/g glyph. prod.)	27.23	37.72	45.01	54.57	61.14								
NMG (mg/g glyph. prod.)	0	0.98	1.23	1.77	2								
Pt in soln. (µg/g glyph. prod.)	3.83	3.36	3.54	3.44	3.32								
% of Fe Lost	86	3.2	1.4	1.8	1.4								

Example 18.   **Preparation of a Pt/Fe/Sn on Carbon Catalyst**

Approximately 10 grams of an activated carbon was slurried in about 90 ml of water. Next, about 0.2 g of $SnCl_2 \cdot 2H_2O$ was dissolved in 250 ml of 0.025 M HCl. The

5   solution was added dropwise to the carbon slurry. After all the solution was added, the slurry was stirred for 3 hr. The pH then was slowly adjusted to 9.0 with a diluted NaOH solution (i.e., a 1.0 to 2.5 molar solution of NaOH), and the slurry was stirred for a few more hours. Next, the slurry was

10   filtered and washed with a plentiful amount of water until the filtrate reached a constant conductivity. The wet cake was dried at 125°C under vacuum. This produced 0.9 wt.% tin on carbon. About 6 grams of this 0.9 wt.% tin on carbon was slurried in about 500 ml of water. Then approximately 0.23

15   grams of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.85 grams of H_2PtCl_6 were co-dissolved in about 150 ml of water and added dropwise to the slurry. After all the solution was added, the slurry was stirred for 4 hours, and then filtered to remove excess iron (~80 wt.%). The wet cake was re-slurried in 480 ml of water.

20   After the pH of the slurry was adjusted to 9-10 with the dilute NaOH solution, the slurry was stirred for a few more hours. Next, the slurry was filtered and washed with a plentiful amount of water until the filtrate reached a constant conductivity. The wet cake was dried at 125°C under

25   vacuum. This produced a catalyst containing 4.9 wt.% Pt, 0.9 wt.% tin and 0.1 wt.% iron on carbon upon high-temperature reduction by heating at 700-750°C in 20% H_2 and 80% Ar for 1-6 hr.

Example 19.   Electr n Microscopy Characterization of Catalysts

Electron microscopy techniques were used to analyze
5   the size, spacial distribution, and composition of the metal
particles of catalysts prepared in Example 17.   Before
analyzing the catalyst, the catalyst was first embedded in an
EM Bed 812 resin (Electron Microscopy Sciences, Fort
Washington, PA).   The resin was then polymerized at about 60°C
10 for approximately 24 hr.   The resulting cured block was
ultramicrotomed into slices having a thickness of about 50 nm.
These slices were then transferred to 200 mesh copper grids
for electron microscopy observation.

High-resolution analytical electron microscopy
15 experiments were carried out in a Vacuum Generators dedicated
scanning transmission electron microscope (model no. VG HB501,
Vacuum Generators, East Brinstead, Sussex, England) with an
image resolution of less than 0.3 nm.   The microscope was
operated at 100 kV.   The vacuum in the specimen chamber area
20 was below about 10^{-6} Pa.   A digital image acquisition system
(ES Vision Data Acquisition System, EmiSpec Sys., Inc., Tempe,
AZ) was used to obtain high-resolution electron microscopy
images.   A windowless energy dispersive X-ray spectrometer
(Link LZ-5 EDS Windowless Detector, Model E5863, High Wycombe,
25 Bucks, England) was used to acquire high energy resolution X-
ray spectra from individual metal particles.   Because of its
high atomic-number sensitivity, high-angle annular dark-field
(HAADF) microscopy was used to observe the metal particles.
An electron probe size of less than about 0.5 nm was used to
30 obtain the HAADF images, and a probe size of less than about 1
nm was used to obtain high energy resolution X-ray spectra.

*   *

The present invention is not limited to the above embodiments and can be variously modified. The above description of the preferred embodiment is intended only to acquaint others skilled in the art with the invention, its
5 principles, and its practical application so that others skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use.

We claim:

1. An oxidation catalyst comprising a carbon support having a noble metal at a surface of the carbon support, the catalyst being characterized as yielding no more than about 0.7 mmole of carbon monoxide per gram of catalyst when a dry
5 sample of the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

2. The oxidation catalyst of claim 1 wherein said carbon monoxide yield is no greater than about 0.5 mmole of carbon monoxide per gram of catalyst.

3. The oxidation catalyst of claim 1 wherein said carbon monoxide yield is no greater than about 0.3 mmole of carbon monoxide per gram of catalyst.

4. An oxidation catalyst comprising a carbon support having a noble metal and a promoter at a surface of the carbon support, the catalyst being characterized as yielding no more than about 0.7 mmole of carbon monoxide per gram of catalyst
5 when a dry sample of the catalyst, after being heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere from about 20 to about 900°C at a rate of about
10 10°C per minute, and then at about 900°C for about 30 minutes.

5. The oxidation catalyst of claim 4 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

6. The oxidation catalyst of claim 4 wherein the promoter is more easily oxidized than the noble metal.

7. The oxidation catalyst of claim 4 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5   cerium, zinc, and zirconium.

8. The oxidation catalyst of claim 4 wherein the promoter comprises tin.

9. The oxidation catalyst of claim 4 wherein the promoter comprises iron.

10. The oxidation catalyst of claim 4 wherein the promoter comprises titanium.

11. The oxidation catalyst of claim 4 wherein at least two promoters are at the surface of the carbon support.

12. The oxidation catalyst of claim 11 wherein the promoters comprise iron and tin.

13. The oxidation catalyst of claim 4 wherein noble metal atoms at the surface are alloyed with the promoter.

14. The oxidation catalyst of claim 4 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

15. The oxidation catalyst of claim 4 wherein
substantially all of the noble metal atoms at the surface are
alloyed with the promoter.

16. The oxidation catalyst of claim 4 wherein said
carbon monoxide yield is no greater than about 0.5 mmole of
carbon monoxide per gram of catalyst.

17. The oxidation catalyst of claim 4 wherein said
carbon monoxide yield is no greater than about 0.3 mmole of
carbon monoxide per gram of catalyst.

18. An oxidation catalyst comprising a carbon support
having a noble metal, carbon, and oxygen at a surface of the
carbon support, wherein the ratio of carbon atoms to oxygen
atoms at the surface is at least about 30:1 as measured by x-
5 ray photoelectron spectroscopy.

19. The oxidation catalyst of claim 18 wherein said
ratio of carbon atoms to oxygen atoms is at least about 40:1.

20. The oxidation catalyst of claim 18 wherein said
ratio of carbon atoms to oxygen atoms is at least about 50:1.

21. The oxidation catalyst of claim 18 wherein said
ratio of carbon atoms to oxygen atoms is at least about 60:1.

22. The oxidation catalyst of claim 18 wherein the ratio
of oxygen atoms to noble metal atoms at the surface is less
than 7:1 as measured by x-ray photoelectron spectroscopy.

23. The oxidation catalyst of claim 22 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

24. The oxidation catalyst of claim 22 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

25. An oxidation catalyst comprising a carbon support having a noble metal, a promoter, carbon, and oxygen at a surface of the carbon support, wherein the catalyst is characterized as having a ratio of carbon atoms to oxygen atoms of at least about 30:1 at the surface as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

26. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

27. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

28. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

29. The oxidation catalyst of claim 25 wherein the catalyst is further characterized as having a ratio of oxygen atoms to noble metal atoms at the surface which is less than 7:1 after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the

catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

30.   The oxidation catalyst of claim 29 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

31.   The oxidation catalyst of claim 29 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

32.   The oxidation catalyst of claim 25 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

33.   The oxidation catalyst of claim 25 wherein the promoter is more easily oxidized than the noble metal.

34.   The oxidation catalyst of claim 25 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium, 5 cerium, zinc, and zirconium.

35.   The oxidation catalyst of claim 25 wherein the promoter comprises tin.

36.   The oxidation catalyst of claim 25 wherein the promoter comprises iron.

37.   The oxidation catalyst of claim 25 wherein the promoter comprises titanium.

38.   The oxidation catalyst of claim 25 wherein at least two promoters are at the surface of the carbon support.

39.   The oxidation catalyst of claim 38 wherein the promoters comprise iron and tin.

40.   The oxidation catalyst of claim 25 wherein noble metal atoms at the surface are alloyed with the promoter.

41.   The oxidation catalyst of claim 25 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

42.   The oxidation catalyst of claim 25 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

43.   An oxidation catalyst comprising a carbon support comprising:
        a noble metal at a surface of the carbon support; and
        a surface layer which (a) has a thickness of about 50 Å
5 as measured inwardly from the surface, and (b) comprises oxygen and carbon, the ratio of carbon atoms to oxygen atoms in the surface layer being at least about 30:1.

44.   The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

45.   The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

46. The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

47. The oxidation catalyst of claim 43 wherein the ratio of oxygen atoms to noble metal atoms in the surface layer is less than 7:1 as measured by x-ray photoelectron spectroscopy.

48. The oxidation catalyst of claim 47 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

49. The oxidation catalyst of claim 47 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

50. An oxidation catalyst comprising a carbon support comprising:

a noble metal and a promoter at a surface of the carbon support, and

5   a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising carbon and oxygen,

wherein the catalyst is characterized as having a ratio of carbon atoms to oxygen atoms in the surface layer of least

10   about 30:1 as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

51. The oxidation catalyst of claim 50 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

98

52.   The oxidation catalyst of claim 50 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

53.   The oxidation catalyst of claim 50 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

54.   The oxidation catalyst of claim 50 wherein the catalyst is further characterized as having a ratio of oxygen atoms to noble metal atoms in the surface layer of less than 7:1 after the catalyst is heated at a temperature of about
5   500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

55.   The oxidation catalyst of claim 54 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

56.   The oxidation catalyst of claim 54 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

57.   The oxidation catalyst of claim 50 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

58.   The oxidation catalyst of claim 50 wherein the promoter is more easily oxidized than the noble metal.

59.   The oxidation catalyst of claim 50 wherein the promoter comprises a metal selected from the group consisting

99

of tin, bismuth, lead, cadmium, magnesium, manganese, nickel,
aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

60.   The oxidation catalyst of claim 50 wherein the
promoter comprises tin.

61.   The oxidation catalyst of claim 50 wherein the
promoter comprises iron.

62.   The oxidation catalyst of claim 50 wherein the
promoter comprises titanium.

63.   The oxidation catalyst of claim 50 wherein at least
two promoters are at the surface of the carbon support.

64.   The oxidation catalyst of claim 63 wherein the
promoters comprise iron and tin.

65.   The oxidation catalyst of claim 50 wherein noble
metal atoms at the surface are alloyed with the promoter.

66.   The oxidation catalyst of claim 50 wherein a
majority of the noble metal atoms at the surface are alloyed
with the promoter.

67.   The oxidation catalyst of claim 50 wherein
substantially all of the noble metal atoms at the surface are
alloyed with the promoter.

68.   An oxidation catalyst prepared by a process
comprising depositing a noble metal at a surface of a carbon

support, and then heating the surface at a temperature greater than about 500°C.

69.   The oxidation catalyst of claim 68 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

70.   The oxidation catalyst of claim 69 wherein the promoter is more easily oxidized than the noble metal.

71.   The oxidation catalyst of claim 69 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium, 5 cerium, zinc, and zirconium.

72.   The oxidation catalyst of claim 69 wherein the promoter comprises tin.

73.   The oxidation catalyst of claim 69 wherein the promoter comprises iron.

74.   The oxidation catalyst of claim 69 wherein the promoter comprises titanium.

75.   The oxidation catalyst of claim 69 wherein at least two promoters are at the surface of the carbon support.

76.   The oxidation catalyst of claim 75 wherein the promoters comprise iron and tin.

77. The oxidation catalyst of claim 69 wherein noble metal atoms at the surface are alloyed with the promoter.

78. The oxidation catalyst of claim 69 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

79. The oxidation catalyst of claim 69 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

80. The oxidation catalyst of claim 68 wherein said temperature is from about 550 to about 1,200°C.

81. The oxidation catalyst of claim 68 wherein said temperature is from about 550 to about 900°C.

82. The oxidation catalyst of claim 68 wherein said heating is conducted in a non-oxidizing environment.

83. The oxidation catalyst of claim 82 wherein said non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N_2 and the noble gases.

84. The oxidation catalyst of claim 82 wherein said temperature is from about 550 to about 1,200°C.

85. The oxidation catalyst of claim 82 wherein the non-oxidizing environment comprises a reducing environment.

86. The oxidation catalyst of claim 85 wherein said temperature is from about 550 to about 1,200°C.

87.   The oxidation catalyst of claim 85 wherein said reducing environment comprises H_2.

88.   An oxidation catalyst prepared by a process comprising depositing a noble metal at a surface of a carbon support, and then heating the surface at a temperature of at least about 400°C, wherein

5   before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

89.   The oxidation catalyst of claim 88 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

90.   The oxidation catalyst of claim 89 wherein the promoter is more easily oxidized than the noble metal.

91.   The oxidation catalyst of claim 89 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,

5   cerium, zinc, and zirconium.

92.· The oxidation catalyst of claim 89 wherein the promoter comprises tin.

93.   The oxidation catalyst of claim 89 wherein the promoter comprises iron.

94.   The oxidation catalyst of claim 89 wherein the promoter comprises titanium.

95.   The oxidation catalyst of claim 89 wherein at least two promoters are at the surface of the carbon support.

96.   The oxidation catalyst of claim 95 wherein the promoters comprise iron and tin.

97.   The oxidation catalyst of claim 89 wherein noble metal atoms at the surface are alloyed with the promoter.

98.   The oxidation catalyst of claim 89 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

99.   The oxidation catalyst of claim 89 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

100.   The oxidation catalyst of claim 88 wherein said temperature is at least about 500°C.

101.   The oxidation catalyst of claim 88 wherein said temperature is from about 550 to about 1,200°C.

102.   The oxidation catalyst of claim 88 wherein said temperature is from about 550 to about 900°C.

103.   The oxidation catalyst of claim 88 wherein the heating is conducted in a non-oxidizing environment.

104. The oxidation catalyst of claim 103 wherein said temperature is at least about 500°C.

105. The oxidation catalyst of claim 103 wherein said temperature is from about 550 to about 1,200°C.

106. The oxidation catalyst of claim 103 wherein the non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N_2 and the noble metals.

107. The oxidation catalyst of claim 103 wherein the non-oxidizing environment comprises a reducing environment.

108. The oxidation catalyst of claim 107 wherein said temperature is at least about 500°C.

109. The oxidation catalyst of claim 107 wherein said temperature is from about 550 to about 1,200°C.

110. The oxidation catalyst of claim 107 wherein the reducing environment comprises H_2.

111. An oxidation catalyst prepared by a process comprising depositing a noble metal at a surface of a carbon support, and then exposing the surface to a reducing environment, wherein

5   before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at

the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

112. The oxidation catalyst of claim 111 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

113. The oxidation catalyst of claim 112 wherein the promoter is more easily oxidized than the noble metal.

114. The oxidation catalyst of claim 112 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

115. The oxidation catalyst of claim 112 wherein the promoter comprises tin.

116. The oxidation catalyst of claim 112 wherein the promoter comprises iron.

117. The oxidation catalyst of claim 112 wherein the promoter comprises titanium.

118. The oxidation catalyst of claim 112 wherein at least two promoters are at the surface of the carbon support.

119. The oxidation catalyst of claim 118 wherein the promoters comprise iron and tin.

120.   The oxidation catalyst of claim 112 wherein noble metal atoms at the surface are alloyed with the promoter.

121.   The oxidation catalyst of claim 112 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

122.   The oxidation catalyst of claim 112 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

123.   The oxidation catalyst of claim 111 wherein the reducing environment comprises ammonia.

124.   The oxidation catalyst of claim 111 wherein the reducing environment comprises $NaBH_4$.

125.   A process for the preparation of an oxidation catalyst, the process comprising depositing a noble metal at a surface of a carbon support, and then heating the surface at a temperature greater than about 500°C.

126.   The process of claim 125 wherein said temperature is from about 550 to about 1,200°C.

127.   The process of claim 125 wherein said temperature is from about 550 to about 900°C.

128.   The process of claim 125 wherein said heating is conducted in a non-oxidizing environment.

129.   The process of claim 128 wherein said temperature is from about 550 to about 1,200°C.

130.   The process of claim 128 wherein the non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N₂ and the noble gases.

131.   The process of claim 128 wherein the non-oxidizing environment comprises a reducing environment.

132.   The process of claim 131 wherein said temperature is from about 550 to about 1,200°C.

133.   The process of claim 131 wherein the reducing environment comprises H₂.

134.   The process of claim 125 further comprising exposing the surface of the carbon support to ammonia.

135.   The process of claim 125 further comprising contacting the surface of the carbon support with a solution comprising ammonium ions.

136.   The process of claim 135 wherein the surface of the carbon support is contacted with a solution comprising ammonium ions after the noble metal is deposited at the surface.

137.   The process of claim 125 further comprising contacting the surface of the carbon support with NaBH₄.

138. The process of claim 125 further comprising removing oxygen from the surface of the carbon support before the noble metal is deposited at the surface.

139. The process of claim 125 wherein the noble metal is deposited at the surface of the carbon support using a noble metal precursor which comprises the noble metal in an oxidation state which is less than the maximum oxidation state of the noble metal.

140. The process of claim 125 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

141. The process of claim 140 wherein the promoter is more easily oxidized than the noble metal.

142. The process of claim 140 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium, cerium, zinc, and zirconium.

143. The process of claim 140 wherein the promoter comprises tin.

144. The process of claim 140 wherein the promoter comprises iron.

145. The process of claim 140 wherein the promoter comprises titanium.

146. The process of claim 140 wherein at least two promoters are deposited at the surface of the carbon support.

147. The process of claim 146 wherein the promoters comprise iron and tin.

148. The process of claim 140 wherein noble metal atoms at the surface are alloyed with the promoter.

149. The process of claim 140 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

150. The process of claim 140 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

151. A process for the preparation of an oxidation catalyst from a carbon support having carbon and oxygen at a surface of the carbon support, the process comprising depositing a noble metal at the surface, and then heating the surface at a temperature of at least about 400°C, wherein the ratio of carbon atoms to oxygen atoms at the surface of the carbon support being at least about 20:1 as measured by x-ray photoelectron spectroscopy before the noble metal deposition.

152. The process of claim 151 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

153. The process of claim 152 wherein the promoter is more easily oxidized than the noble metal.

110

154. The process of claim 152 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,

5 cerium, zinc, and zirconium.

155. The process of claim 152 wherein the promoter comprises tin.

156. The process of claim 152 wherein the promoter comprises iron.

157. The process of claim 152 wherein the promoter comprises titanium.

158. The process of claim 152 wherein at least two promoters are deposited at the surface of the carbon support.

159. The process of claim 158 wherein the promoters comprise iron and tin.

160. The process of claim 152 wherein noble metal atoms at the surface are alloyed with the promoter.

161. The process of claim 152 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

162. The process of claim 152 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

163.　The process of claim 151 wherein said temperature is at least about 500°C.

164.　The process of claim 151 wherein said temperature is from about 550 to about 1,200°C.

165.　The process of claim 151 wherein said temperature is from about 550 to about 900°C.

166.　The process of claim 151 wherein said heating is conducted in a non-oxidizing environment.

167.　The process of claim 166 wherein said temperature is at least about 500°C.

168.　The process of claim 166 wherein said temperature is from about 550 to about 1,200°C.

169.　The process of claim 166 wherein the non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N_2 and the noble gases.

170.　The process of claim 166 wherein the non-oxidizing environment comprises a reducing environment.

171.　The process of claim 170 wherein said temperature is at least about 500°C.

172.　The process of claim 170 wherein said temperature is from about 550 to about 1,200°C.

173. The process of claim 170 wherein the reducing environment comprises H_2.

174. A process for the preparation of an oxidation catalyst from a carbon support having carbon and oxygen at a surface of the carbon support, the process comprising depositing a noble metal at the surface, and then exposing the
5 surface to a reducing environment, wherein the ratio of carbon atoms to oxygen atoms at the surface is at least about 20:1 as measured by x-ray photoelectron spectroscopy before the noble metal deposition.

175. The process of claim 174 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

176. The process of claim 175 wherein the promoter is more easily oxidized than the noble metal.

177. The process of claim 175 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

178. The process of claim 175 wherein the promoter comprises tin.

179. The process of claim 175 wherein the promoter comprises iron.

180. The process of claim 175 wherein the promoter comprises titanium.

181. The process of claim 175 wherein at least two promoters are deposited at the surface of the carbon support.

182. The process of claim 181 wherein the promoters comprise iron and tin.

183. The process of claim 175 wherein noble metal atoms at the surface are alloyed with the promoter.

184. The process of claim 175 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

185. The process of claim 175 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

186. The process of claim 174 wherein the reducing environment comprises ammonia.

187. The process of claim 186 further comprising heating the surface to at least about 400°C after the noble metal is deposited.

188. The process of claim 187 wherein said heating is conducted in a non-oxidizing environment.

189. The process of claim 174 wherein the reducing environment comprises NaBH$_4$.

190. The process of claim 189 further comprising heating the surface at a temperature of at least about 400°C after the noble metal is deposited at the surface of the carbon support.

191. The process of claim 190 wherein said heating is conducted in a non-oxidizing environment.

192. A process for the preparation of an oxidation catalyst from a carbon support having carbon and oxygen at a surface of the carbon support, the process comprising depositing a noble metal at the surface, and then exposing the

5 surface to a reducing environment to reduce the surface so that the ratio of carbon atoms to oxygen atoms at the surface is at least about 30:1 as measured by x-ray photoelectron spectroscopy.

193. The process of claim 192 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

194. The process of claim 192 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

195. The process of claim 192 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

196. The process of claim 192 wherein the ratio of oxygen atoms to noble metal atoms at the surface is less than 7:1 as measured by x-ray photoelectron spectroscopy.

197. The process of claim 196 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

198.   The process of claim 196 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

199.   The process of claim 192 wherein the reducing environment comprises ammonia.

200.   The process of claim 192 wherein the reducing environment comprises $NaBH_4$.

201.   The process of claim 192 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

202.   The process of claim 201 wherein the promoter is more easily oxidized than the noble metal.

203.   The process of claim 201 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

204.   The process of claim 201 wherein the promoter comprises tin.

205.   The process of claim 201 wherein the promoter comprises iron.

206.   The process of claim 201 wherein the promoter comprises titanium.

207.   The process of claim 201 wherein at least two promoters are deposited at the surface of the carbon support.

116

208.   The process of claim 207 wherein the promoters comprise iron and tin.

209.   The process of claim 201 wherein noble metal atoms at the surface are alloyed with the promoter.

210.   The process of claim 201 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

211.   The process of claim 201 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

212.   A process for the preparation of an oxidation catalyst, the process comprising depositing a noble metal at a surface of a carbon support, and then exposing the surface to a reducing environment to reduce the surface so that no more
5   than about 0.7 mmole of carbon monoxide per gram of catalyst desorb from the catalyst when a dry sample of the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

213.   The process of claim 212 wherein said carbon monoxide yield is no greater than about 0.5 mmole of carbon monoxide per gram of catalyst.

214.   The process of claim 212 wherein said carbon monoxide yield is no greater than about 0.3 mmole of carbon monoxide per gram of catalyst.

117

215.   The process of claim 212 wherein the reducing environment comprises ammonia.

216.   The process of claim 212 wherein the reducing environment comprises $NaBH_4$.

217.   The process of claim 212 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

218.   The process of claim 217 wherein the promoter is more easily oxidized than the noble metal.

219.   The process of claim 217 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

220.   The process of claim 217 wherein the promoter comprises tin.

221.   The process of claim 217 wherein the promoter comprises iron.

222.   The process of claim 217 wherein the promoter comprises titanium.

223.   The process of claim 217 wherein at least two promoters are deposited at the surface of the carbon support.

224. The process of claim 223 wherein the promoters comprise iron and tin.

225. The process of claim 217 wherein noble metal atoms at the surface are alloyed with the promoter.

226. The process of claim 217 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

227. The process of claim 217 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

228. A process for oxidizing a reagent in a mixture, the mixture being able to solubilize a noble metal, the process comprising contacting the mixture with an oxidation catalyst in the presence of oxygen, wherein the catalyst:

5   comprises a carbon support having a noble metal at a surface of the carbon support; and

       is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst in a helium atmosphere is heated from about 20 to

10   about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

229. The process of claim 228 wherein the process is conducted in a continuous reactor system.

230. The process of claim 228 wherein said carbon monoxide yield is no greater than about 0.7 mmole of carbon monoxide per gram of catalyst.

231.   The process of claim 228 wherein the mixture is acidic.

232.   A process for oxidizing a reagent in a mixture which can solubilize a noble metal, the process comprising contacting the mixture with an oxidation catalyst in the presence of oxygen, wherein the catalyst:

5   comprises a carbon support having a noble metal and a promoter at a surface of the carbon support; and

          is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst, after being heated at a temperature of about 10 500°C for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

233.   The process of claim 232 wherein the process is conducted in a continuous reactor system.

234.   The process of claim 232 wherein said carbon monoxide yield is no greater than about 0.7 mmole of carbon monoxide per gram of catalyst.

235.   The process of claim 232 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

236.   A process for oxidizing a reagent in a mixture which can solubilize a noble metal, the process comprising contacting the mixture with an oxidation catalyst in the

120

presence of oxygen, wherein the catalyst comprises a carbon

5 support having a noble metal, carbon, and oxygen at a surface

of the carbon support, the ratio of carbon atoms to oxygen

atoms at the surface being at least about 20:1 as measured by

x-ray photoelectron spectroscopy.

237. The process of claim 236 wherein the process is

conducted in a continuous reactor system.

238. The process of claim 236 wherein said ratio of

carbon atoms to oxygen atoms is at least about 30:1.

239. A process for oxidizing a reagent in a mixture

which can solubilize a noble metal, the process comprising

contacting the mixture with an oxidation catalyst in the

presence of oxygen, wherein the catalyst:

5   comprises a carbon support having a noble metal, a

promoter, carbon, and oxygen at a surface of the carbon

support; and

is characterized as having a ratio of carbon atoms to

oxygen atoms at the surface which is at least about 20:1 as

10 measured by x-ray photoelectron spectroscopy after the

catalyst is heated at a temperature of about 500°C for about 1

hour in a hydrogen atmosphere and before the catalyst is

exposed to an oxidant following the heating in the hydrogen

atmosphere.

240. The process of claim 239 wherein the process is

conducted in a continuous reactor system.

241. The process of claim 239 wherein said ratio of

carbon atoms to oxygen atoms is at least about 30:1.

242. The process of claim 239 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

243. A process for oxidizing a reagent in a mixture which can solubilize a noble metal, the process comprising contacting the mixture with an oxidation catalyst in the presence of oxygen, wherein the catalyst comprises a carbon
5 support having (a) a noble metal at a surface of the carbon support; and (b) a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising oxygen and carbon, the ratio of carbon atoms to oxygen atoms in the surface layer being at least about 20:1 as measured by
10 x-ray photoelectron spectroscopy.

244. The process of claim 243 wherein the process is conducted in a continuous reactor system.

245. The process of claim 243 wherein said ratio of carbon atoms to oxygen atoms is at least about 30:1.

246. A process for oxidizing a reagent in a mixture which can solubilize a noble metal, the process comprising contacting the mixture with an oxidation catalyst in the presence of oxygen, wherein the catalyst:
5 comprises a carbon support having: (a) a noble metal and a promoter at a surface of the carbon support; and (b) a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising carbon and oxygen; and
10 is characterized as having a ratio of carbon atoms to oxygen atoms in the surface layer of at least about 20:1 as

measured by x-ray photoelectron spectroscopy after the
catalyst is heated at a temperature of about 500°C for about 1
hour in a hydrogen atmosphere and before the catalyst is

15   exposed to an oxidant following the heating in the hydrogen
atmosphere.

247.   The process of claim 246 wherein the process is
conducted in a continuous reactor system.

248.   The process of claim 246 wherein said ratio of
carbon atoms to oxygen atoms is at least about 30:1.

249.   The process of claim 246 wherein at least 0.05% by
weight of the catalyst consists of at least one promoter.

250.   A process for oxidizing a reagent in a mixture
which can solubilize a noble metal, the process comprising:
        forming an oxidation catalyst by a process comprising
depositing a noble metal at a surface of a carbon support, and

5   then heating the surface at a temperature of at least about
400°C; and
        contacting the mixture with the oxidation catalyst in the
presence of oxygen.

251.   The process of claim 250 wherein the mixture is
contacted with the oxidation catalyst in the presence of
oxygen in a continuous reactor system.

252.   The process of claim 250 wherein at least 0.05% by
weight of the catalyst consists of at least one promoter.

123

253. The process of claim 252 wherein the promoter is more easily oxidized than the noble metal.

254. The process of claim 252 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium, cerium, zinc, and zirconium.

255. The process of claim 252 wherein the promoter comprises tin.

256. The process of claim 252 wherein the promoter comprises iron.

257. The process of claim 252 wherein the promoter comprises titanium.

258. The process of claim 252 wherein at least two promoters are deposited at the surface of the carbon support.

259. The process of claim 258 wherein the promoters comprise iron and tin.

260. The process of claim 252 wherein noble metal atoms at the surface are alloyed with the promoter.

261. The process of claim 252 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

262. The process of claim 252 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

263. The process of claim 250 wherein said temperature is at least about 500°C.

264. The process of claim 250 wherein, before the noble metal deposition, the carbon support has carbon and oxygen at a surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least

5 about 20:1 as measured by x-ray photoelectron spectroscopy.

265. The process of claim 250 wherein said heating is conducted in a non-oxidizing environment.

266. The process of claim 265 wherein the non-oxidizing environment comprises a reducing environment.

267. The process of claim 266 wherein the reducing environment comprises H_2.

268. A process for oxidizing a reagent in a mixture which can solubilize a noble metal, the process comprising:
    forming an oxidation catalyst by a process comprising:
    (a) depositing a noble metal at a surface of a carbon support,

5 and (b) exposing the surface to a reducing environment; and
    contacting the mixture with the oxidation catalyst in the presence of oxygen,
    wherein, before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon

10 support in amounts such that the ratio of carbon atoms to

125

oxygen atoms at the surface is at least 20:1 as measured by x-ray photoelectron spectroscopy.

269. The process of claim 268 wherein the mixture is contacted with the oxidation catalyst in the presence of oxygen in a continuous reactor system.

270. The process of claim 268 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

271. The process of claim 270 wherein the promoter is more easily oxidized than the noble metal.

272. The process of claim 270 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium, 5 cerium, zinc, and zirconium.

273. The process of claim 270 wherein the promoter comprises tin.

274. The process of claim 270 wherein the promoter comprises iron.

275. The process of claim 270 wherein the promoter comprises titanium.

276. The process of claim 270 wherein at least two promoters are deposited at the surface of the carbon support.

277.   The process of claim 276 wherein the promoters comprise iron and tin.

278.   The process of claim 270 wherein noble metal atoms at the surface are alloyed with the promoter.

279.   The process of claim 270 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

280.   The process of claim 270 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

281.   A process for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the process comprising contacting N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxidation catalyst in the presence of
5   oxygen, wherein the catalyst:
comprises a carbon support having a noble metal at a surface of the carbon support; and
is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of
10   the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

282.   The process of claim 281 wherein the process is conducted in a continuous reactor system.

283.   The process of claim 281 wherein said carbon
monoxide yield is no greater than about 0.7 mmole of carbon
monoxide per gram of catalyst.

284.   The process of claim 281 wherein said carbon
monoxide yield is no greater than about 0.5 mmole of carbon
monoxide per gram of catalyst.

285.   The process of claim 281 wherein said carbon
monoxide yield is no greater than about 0.3 mmole of carbon
monoxide per gram of catalyst.

286.   The process of claim 281 wherein the oxidation is
conducted in a solution or slurry, and oxygen is introduced
into the solution or slurry at a rate such that at least about
40% of the oxygen is utilized.

287.   The process of claim 281 wherein the oxidation is
conducted in a solution or slurry, and oxygen is introduced
into the solution or slurry at a rate such that at least about
60% of the oxygen is utilized.

288.   The process of claim 281 wherein the oxidation is
conducted in a solution or slurry, and oxygen is introduced
into the solution or slurry at a rate such that at least about
80% of the oxygen is utilized.

289.   The process of claim 281 wherein the oxidation is
conducted in a solution or slurry, and oxygen is introduced
into the solution or slurry at a rate such that at least about
90% of the oxygen is utilized.

290. The process of claim 281 wherein the oxidation is conducted in a solution or slurry, and oxygen is introduced into the solution or slurry at a rate such that at least about 40% of the oxygen is utilized until at least about 80% of the

5   reagent has been consumed, and then introduced into the solution or slurry at a reduced rate to enhance oxidation of formaldehyde in the solution or slurry.

291. The process of claim 281 further comprising introducing a sacrificial reducing agent into the solution or slurry.

292. The process of claim 291 wherein the sacrificial reducing agent comprises formaldehyde, formic acid, or a combination thereof.

293. A process for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the process comprising contacting N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxidation catalyst in the presence of

5   oxygen, wherein the catalyst comprises a carbon support having a noble metal, carbon, and oxygen at a surface of the carbon support, the ratio of carbon atoms to oxygen atoms at the surface being at least about 20:1 as measured by x-ray photoelectron spectroscopy.

294. The process of claim 293 wherein the process is conducted in a continuous reactor system.

295. The process of claim 293 wherein said ratio of carbon atoms to oxygen atoms is at least about 30:1.

129

296. The process of claim 293 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

297. The process of claim 293 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

298. The process of claim 293 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

299. The process of claim 293 wherein the ratio of oxygen atoms to noble metal atoms at the surface is less than about 8:1 as measured by x-ray photoelectron spectroscopy.

300. The process of claim 299 wherein said ratio of oxygen atoms to noble metal atoms is less than about 7:1.

301. The process of claim 299 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

302. The process of claim 299 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

303. A process for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the process comprising contacting N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxidation catalyst in the presence of
5 oxygen, wherein the catalyst comprises a carbon support comprising: (a) a noble metal at a surface of the carbon support; and (b) a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising carbon and oxygen, the ratio of carbon atoms to oxygen atoms

10   in the surface layer being at least about 2υ:1 as measured by
     x-ray photoelectron spectroscopy.

     304.   The process of claim 303 wherein the process is
conducted in a continuous reactor system.

     305.   The process of claim 303 wherein said ratio of
carbon atoms to oxygen atoms is at least about 30:1.

     306.   The process of claim 303 wherein said ratio of
carbon atoms to oxygen atoms is at least about 40:1.

     307.   The process of claim 303 wherein said ratio of
carbon atoms to oxygen atoms is at least about 50:1.

     308.   The process of claim 303 wherein said ratio of
carbon atoms to oxygen atoms is at least about 60:1.

     309.   The process of claim 303 wherein the ratio of
oxygen atoms to noble metal atoms in the surface layer is less
than about 8:1 as measured by x-ray photoelectron
spectroscopy.

     310.   The process of claim 309 wherein said ratio of
oxygen atoms to noble metal atoms is less than about 7:1.

     311.   The process of claim 309 wherein said ratio of
oxygen atoms to noble metal atoms is less than about 6:1.

     312.   The process of claim 309 wherein said ratio of
oxygen atoms to noble metal atoms is less than about 5:1.

313.   A process for the preparation of N-
(phosphonomethyl)glycine or a salt thereof, the process
comprising:

        forming an oxidation catalyst by a process comprising
5   depositing a noble metal at a surface of a carbon support, and
then heating the surface at a temperature of at least about
400°C; and

        contacting N-(phosphonomethyl)iminodiacetic acid or a
salt thereof with the oxidation catalyst in the presence of
10 oxygen.

        314.   The process of claim 313 wherein the N-
(phosphonomethyl)iminodiacetic acid or a salt thereof is
contacted with the oxidation catalyst in the presence of
oxygen in a continuous reactor system.

        315.   The process of claim 313 wherein said temperature
is at least about 500°C.

        316.   The process of claim 313 wherein said temperature
is from about 550 to about 1,200°C.

        317.   The process of claim 313 wherein said temperature
is from about 550 to about 900°C.

        318.   The process of claim 313 wherein, before the noble
metal deposition, the carbon support has carbon and oxygen at
the surface of the carbon support in amounts such that the
ratio of carbon atoms to oxygen atoms at the surface is at
5   least about 20:1 as measured by x-ray photoelectron
spectroscopy.

319. The process of claim 313 wherein said heating is conducted in a non-oxidizing environment.

320. The process of claim 319 wherein said temperature is at least about 500°C.

321. The process of claim 319 wherein said temperature is from about 550 to about 1,200°C.

322. The process of claim 319 wherein the non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N_2 and the noble gases.

323. The process of claim 319 wherein, before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at the surface before
5   the noble metal deposition is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

324. The process of claim 319 wherein the non-oxidizing environment comprises a reducing environment.

325. The process of claim 324 wherein said temperature is at least about 500°C.

326. The process of claim 324 wherein said temperature is from about 550 to about 1,200°C.

327. The process of claim 324 wherein the reducing environment comprises H_2.

328. The process of claim 324 wherein, before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at the surface before

5 the noble metal deposition is at least about 20:1 as measured by x-ray photoelectron spectroscopy.

329. A process for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the process comprising:

forming an oxidation catalyst by a process comprising:

5 (a) depositing a noble metal at a surface of a carbon support, and (b) exposing the surface to a reducing environment; and

contacting N-(phosphonomethyl)iminodiacetic acid or a salt thereof with the oxidation catalyst in the presence of oxygen,

10 wherein, before the noble metal deposition, the carbon support has carbon and oxygen at the surface of the carbon support in amounts such that the ratio of carbon atoms to oxygen atoms at the surface is at least 20:1 as measured by x-ray photoelectron spectroscopy.

330. The process of claim 329 wherein the N-(phosphonomethyl)iminodiacetic acid or a salt thereof is contacted with the oxidation catalyst in the presence of oxygen in a continuous reactor system.

331. The process of claim 329 wherein the reducing environment comprises ammonia.

332. The process of claim 329 wherein the reducing environment comprises $NaBH_4$.

333. A process for the preparation of N-
(phosphonomethyl)glycine or a salt thereof, the process
comprising contacting, in the presence of oxygen, N-
(phosphonomethyl)iminodiacetic acid or a salt thereof with a
5 catalyst comprising a carbon support having a noble metal, a
promoter, carbon, and oxygen at a surface of the carbon
support.

334. The process of claim 333 wherein the process is
contacted in a continuous reactor system.

335. The process of claim 333 wherein at least 0.05% by
weight of the catalyst consists of at least one promoter.

336. The process of claim 333 wherein the promoter is
more easily oxidized than the noble metal.

337. The process of claim 333 wherein the promoter
comprises a metal selected from the group consisting of tin,
bismuth, lead, cadmium, magnesium, manganese, nickel,
aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5 cerium, zinc, and zirconium.

338. The process of claim 333 wherein the promoter
comprises tin.

339. The process of claim 333 wherein the promoter
comprises iron.

340. The process of claim 333 wherein the promoter
comprises titanium.

135

341.   The process of claim 333 wherein at least two promoters are at the surface of the carbon support.

342.   The process of claim 341 wherein the promoters comprise iron and tin.

343.   The process of claim 333 wherein noble metal atoms at the surface are alloyed with the promoter.

344.   The process of claim 333 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

345.   The process of claim 333 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

346.   The process of claim 333 wherein the catalyst is characterized as having a ratio of carbon atoms to oxygen atoms at the surface which is at least about 20:1 as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

347.   The process of claim 346 wherein said ratio of carbon atoms to oxygen atoms is at least about 30:1.

348.   The process of claim 346 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

349.   The process of claim 346 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

350.   The process of claim 346 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

351.   The process of claim 346 wherein the catalyst is further characterized as having a ratio of oxygen atoms to noble metal atoms at the surface which is less than about 8:1 after the catalyst is heated at a temperature of about 500°C

5   for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

352.   The process of claim 351 wherein said ratio of oxygen atoms to noble metal atoms is less than about 7:1.

353.   The process of claim 351 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

354.   The process of claim 351 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

355.   The process of claim 333 wherein the catalyst is characterized as yielding no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst, after being heated at a temperature of about 500°C

5   for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

356. The process of claim 355 wherein said carbon monoxide yield is no greater than about 0.7 mmole of carbon monoxide per gram of catalyst.

357. The process of claim 355 wherein said carbon monoxide yield is no greater than about 0.5 mmole of carbon monoxide per gram of catalyst.

358. The process of claim 355 wherein said carbon monoxide yield is no greater than about 0.3 mmole of carbon monoxide per gram of catalyst.

359. A process for the preparation of N-(phosphonomethyl)glycine or a salt thereof, the process comprising contacting N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxidation catalyst in the presence of
5 oxygen, wherein the catalyst comprises a carbon support having: (a) a noble metal and a promoter at a surface of the carbon support; and (b) a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising carbon and oxygen, the catalyst being characterized
10 as having a ratio of carbon atoms to oxygen atoms in the surface layer which is at least about 20:1 as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant
15 following the heating in the hydrogen atmosphere.

360. The process of claim 359 wherein the process is contacted in a continuous reactor system.

361. The process of claim 359 wherein said ratio of carbon atoms to oxygen atoms is at least about 30:1.

362. The process of claim 359 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

363. The process of claim 359 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

364. The process of claim 359 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

365. The process of claim 359 wherein the catalyst is further characterized as having a ratio of oxygen atoms to noble metal atoms in the surface layer which is less than about 8:1 after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

366. The process of claim 365 wherein said ratio of oxygen atoms to noble metal atoms is less than about 7:1.

367. The process of claim 365 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

368. The process of claim 365 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

369. The process of claim 359 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

370.   The process of claim 359 wherein the promoter is more easily oxidized than the noble metal.

371.   The process of claim 359 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, rhenium,
5   cerium, zinc, and zirconium.

372.   The process of claim 359 wherein the promoter comprises tin.

373.   The process of claim 359 wherein the promoter comprises iron.

374.   The process of claim 359 wherein the promoter comprises titanium.

375.   The process of claim 359 wherein at least two promoters are at the surface of the carbon support.

376.   The process of claim 375 wherein the promoters comprise iron and tin.

377.   The process of claim 359 wherein noble metal atoms at the surface are alloyed with the promoter.

378.   The process of claim 359 wherein a majority of the noble metals at the surface are alloyed with the promoter.

379. The process of claim 359 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

AMENDED CLAIMS

1. An oxidation catalyst comprising a non-graphitic carbon support having a noble metal at a surface of the non-graphitic carbon support, the catalyst being characterized as yielding no more than about 0.7 mmole of carbon monoxide per
5 gram of catalyst when a dry sample of the catalyst in a helium atmosphere is heated from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

2. The oxidation catalyst of claim 1 wherein said carbon monoxide yield is no greater than about 0.5 mmole of carbon monoxide per gram of catalyst.

3. The oxidation catalyst of claim 1 wherein said carbon monoxide yield is no greater than about 0.3 mmole of carbon monoxide per gram of catalyst.

4. An oxidation catalyst comprising a non-graphitic carbon support having a noble metal and a promoter at a surface of the non-graphitic carbon support, the catalyst being characterized as yielding no more than about 0.7 mmole
5 of carbon monoxide per gram of catalyst when a dry sample of the catalyst, after being heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere from
10 about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes.

5. The oxidation catalyst of claim 4 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

142

AMENDED SHEET (ARTICLE 19)

6. The oxidation catalyst of claim 4 wherein the promoter is more easily oxidized than the noble metal.

7. The oxidation catalyst of claim 4 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron, 5 rhenium, cerium, zinc, and zirconium.

8. The oxidation catalyst of claim 4 wherein the promoter comprises tin.

9. The oxidation catalyst of claim 4 wherein the promoter comprises iron.

10. The oxidation catalyst of claim 4 wherein the promoter comprises titanium.

11. The oxidation catalyst of claim 4 wherein at least two promoters are at the surface of the non-graphitic carbon support.

12. The oxidation catalyst of claim 11 wherein the promoters comprise iron and tin.

13. The oxidation catalyst of claim 4 wherein noble metal atoms at the surface are alloyed with the promoter.

14. The oxidation catalyst of claim 4 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

143

AMENDED SHEET (ARTICLE 19)

15. The oxidation catalyst of claim 4 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

16. The oxidation catalyst of claim 4 wherein said carbon monoxide yield is no greater than about 0.5 mmole of carbon monoxide per gram of catalyst.

17. The oxidation catalyst of claim 4 wherein said carbon monoxide yield is no greater than about 0.3 mmole of carbon monoxide per gram of catalyst.

18. An oxidation catalyst comprising a non-graphitic carbon support having a noble metal, carbon, and oxygen at a surface of the non-graphitic carbon support, wherein the ratio of carbon atoms to oxygen atoms at the surface is at least about 30:1 as measured by x-ray photoelectron spectroscopy.

19. The oxidation catalyst of claim 18 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

20. The oxidation catalyst of claim 18 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

21. The oxidation catalyst of claim 18 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

22. The oxidation catalyst of claim 18 wherein the ratio of oxygen atoms to noble metal atoms at the surface is less than 7:1 as measured by x-ray photoelectron spectroscopy.

23. The oxidation catalyst of claim 22 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

24. The oxidation catalyst of claim 22 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

25. An oxidation catalyst comprising a non-graphitic carbon support having a noble metal, a promoter, carbon, and oxygen at a surface of the non-graphitic carbon support, wherein the catalyst is characterized as having a ratio of

5 carbon atoms to oxygen atoms of at least about 30:1 at the surface as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the

10 hydrogen atmosphere.

26. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

27. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

28. The oxidation catalyst of claim 25 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

29. The oxidation catalyst of claim 25 wherein the catalyst is further characterized as having a ratio of oxygen atoms to noble metal atoms at the surface which is less than 7:1 after the catalyst is heated at a temperature of about

5 500°C for about 1 hour in a hydrogen atmosphere and before the

145

38.   The oxidation catalyst of claim 25 wherein at least two promoters are at the surface of the non-graphitic carbon support.

39.   The oxidation catalyst of claim 38 wherein the promoters comprise iron and tin.

40.   The oxidation catalyst of claim 25 wherein noble metal atoms at the surface are alloyed with the promoter.

41.   The oxidation catalyst of claim 25 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

42.   The oxidation catalyst of claim 25 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

43.   An oxidation catalyst comprising a non-graphitic carbon support comprising:
      a noble metal at a surface of the non-graphitic carbon support; and
5   a surface layer which (a) has a thickness of about 50 Å as measured inwardly from the surface, and (b) comprises oxygen and carbon, the ratio of carbon atoms to oxygen atoms in the surface layer being at least about 30:1.

44.   The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

45.   The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 50:1.

146

46.   The oxidation catalyst of claim 43 wherein said ratio of carbon atoms to oxygen atoms is at least about 60:1.

47.   The oxidation catalyst of claim 43 wherein the ratio of oxygen atoms to noble metal atoms in the surface layer is less than 7:1 as measured by x-ray photoelectron spectroscopy.

48.   The oxidation catalyst of claim 47 wherein said ratio of oxygen atoms to noble metal atoms is less than about 6:1.

49.   The oxidation catalyst of claim 47 wherein said ratio of oxygen atoms to noble metal atoms is less than about 5:1.

50.   An oxidation catalyst comprising a non-graphitic carbon support comprising:
        a noble metal and a promoter at a surface of the non-graphitic carbon support, and
5   a surface layer having a thickness of about 50 Å as measured inwardly from the surface and comprising carbon and oxygen,
        wherein the catalyst is characterized as having a ratio of carbon atoms to oxygen atoms in the surface layer of least
10   about 30:1 as measured by x-ray photoelectron spectroscopy after the catalyst is heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before the catalyst is exposed to an oxidant following the heating in the hydrogen atmosphere.

51.   The oxidation catalyst of claim 50 wherein said ratio of carbon atoms to oxygen atoms is at least about 40:1.

.147

AMENDED SHEET (ARTICLE 19)

of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron,
5 rhenium, cerium, zinc, and zirconium.

60. The oxidation catalyst of claim 50 wherein the promoter comprises tin.

61. The oxidation catalyst of claim 50 wherein the promoter comprises iron.

62. The oxidation catalyst of claim 50 wherein the promoter comprises titanium.

63. The oxidation catalyst of claim 50 wherein at least two promoters are at the surface of the non-graphitic carbon support.

64. The oxidation catalyst of claim 63 wherein the promoters comprise iron and tin.

65. The oxidation catalyst of claim 50 wherein noble metal atoms at the surface are alloyed with the promoter.

66. The oxidation catalyst of claim 50 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

67. The oxidation catalyst of claim 50 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

68. An oxidation catalyst prepared by a process comprising depositing a noble metal at a surface of a non-graphitic carbon

148

support, and then heating the surface at a temperature greater than about 500°C.

69. The oxidation catalyst of claim 68 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

70. The oxidation catalyst of claim 69 wherein the promoter is more easily oxidized than the noble metal.

71. The oxidation catalyst of claim 69 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron,
5 rhenium, cerium, zinc, and zirconium.

72. The oxidation catalyst of claim 69 wherein the promoter comprises tin.

73. The oxidation catalyst of claim 69 wherein the promoter comprises iron.

74. The oxidation catalyst of claim 69 wherein the promoter comprises titanium.

75. The oxidation catalyst of claim 69 wherein at least two promoters are at the surface of the non-graphitic carbon support.

76. The oxidation catalyst of claim 75 wherein the promoters comprise iron and tin.

149

87.   The oxidation catalyst of claim 85 wherein said
reducing environment comprises H_2.

88.   An oxidation catalyst prepared by a process
comprising depositing a noble metal at a surface of a non-
graphitic carbon support, and then heating the surface at a
temperature of at least about 400°C, wherein

5   before the noble metal deposition, the non-graphitic
carbon support has carbon and oxygen at the surface of the
non-graphitic carbon support in amounts such that the ratio
of carbon atoms to oxygen atoms at the surface is at least
about 20:1 as measured by x-ray photoelectron spectroscopy.

89.   The oxidation catalyst of claim 88 wherein at least
0.05% by weight of the catalyst consists of at least one
promoter.

90.   The oxidation catalyst of claim 89 wherein the
promoter is more easily oxidized than the noble metal.

91.   The oxidation catalyst of claim 89 wherein the
promoter comprises a metal selected from the group consisting
of tin, bismuth, lead, cadmium, magnesium, manganese, nickel,
aluminum, cobalt, titanium, antimony, selenium, iron,
5 rhenium, cerium, zinc, and zirconium.

92.   The oxidation catalyst of claim 89 wherein the
promoter comprises tin.

93.   The oxidation catalyst of claim 89 wherein the
promoter comprises iron.

AMENDED SHEET (ARTICLE 19)

94. The oxidation catalyst of claim 89 wherein the promoter comprises titanium.

95. The oxidation catalyst of claim 89 wherein at least two promoters are at the surface of the non-graphitic carbon support.

96. The oxidation catalyst of claim 95 wherein the promoters comprise iron and tin.

97. The oxidation catalyst of claim 89 wherein noble metal atoms at the surface are alloyed with the promoter.

98. The oxidation catalyst of claim 89 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

99. The oxidation catalyst of claim 89 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

100. The oxidation catalyst of claim 88 wherein said temperature is at least about 500°C.

101. The oxidation catalyst of claim 88 wherein said temperature is from about 550 to about 1,200°C.

102. The oxidation catalyst of claim 88 wherein said temperature is from about 550 to about 900°C.

103. The oxidation catalyst of claim 88 wherein the heating is conducted in a non-oxidizing environment.

151

AMENDED SHEET (ARTICLE 19)

120. The oxidation catalyst of claim 112 wherein noble metal atoms at the surface are alloyed with the promoter.

121. The oxidation catalyst of claim 112 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

122. The oxidation catalyst of claim 112 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

123. The oxidation catalyst of claim 111 wherein the reducing environment comprises ammonia.

124. The oxidation catalyst of claim 111 wherein the reducing environment comprises $NaBH_4$.

125. A process for the preparation of an oxidation catalyst, the process comprising depositing a noble metal at a surface of a non-graphitic carbon support, and then heating the surface at a temperature greater than about 500°C.

126. The process of claim 125 wherein said temperature is from about 550 to about 1,200°C.

127. The process of claim 125 wherein said temperature is from about 550 to about 900°C.

128. The process of claim 125 wherein said heating is conducted in a non-oxidizing environment.

129. The process of claim 128 wherein said temperature is from about 550 to about 1,200°C.

130. The process of claim 128 wherein the non-oxidizing environment consists essentially of at least one gas selected from the group consisting of N_2 and the noble gases.

131. The process of claim 128 wherein the non-oxidizing environment comprises a reducing environment.

132. The process of claim 131 wherein said temperature is from about 550 to about 1,200°C.

133. The process of claim 131 wherein the reducing environment comprises H_2.

134. The process of claim 125 further comprising exposing the surface of the non-graphitic carbon support to ammonia.

135. The process of claim 125 further comprising contacting the surface of the non-graphitic carbon support with a solution comprising ammonium ions.

136. The process of claim 135 wherein the surface of the non-graphitic carbon support is contacted with a solution comprising ammonium ions after the noble metal is deposited at the surface.

137. The process of claim 125 further comprising contacting the surface of the non-graphitic carbon support with $NaBH_4$.

153

AMENDED SHEET (ARTICLE 19)

138.   The process of claim 125 further comprising removing oxygen from the surface of the non-graphitic carbon support before the noble metal is deposited at the surface.

139.   The process of claim 125 wherein the noble metal is deposited at the surface of the non-graphitic carbon support using a noble metal precursor which comprises the noble metal in an oxidation state which is less than the
5 maximum oxidation state of the noble metal.

140.   The process of claim 125 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

141.   The process of claim 140 wherein the promoter is more easily oxidized than the noble metal.

142.   The process of claim 140 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron,
5 rhenium, cerium, zinc, and zirconium.

143.   The process of claim 140 wherein the promoter comprises tin.

144.   The process of claim 140 wherein the promoter comprises iron.

145.   The process of claim 140 wherein the promoter comprises titanium.

146. The process of claim 140 wherein at least two promoters are deposited at the surface of the non-graphitic carbon support.

147. The process of claim 146 wherein the promoters comprise iron and tin.

148. The process of claim 140 wherein noble metal atoms at the surface are alloyed with the promoter.

149. The process of claim 140 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

150. The process of claim 140 wherein substantially all of the noble metal atoms at the surface are alloyed with the promoter.

151. A process for the preparation of an oxidation catalyst from a non-graphitic carbon support having carbon and oxygen at a surface of the non-graphitic carbon support, the process comprising depositing a noble metal at the
5   surface, and then heating the surface at a temperature of at least about 400°C, wherein the ratio of carbon atoms to oxygen atoms at the surface of the non-graphitic carbon support being at least about 20:1 as measured by x-ray photoelectron spectroscopy before the noble metal deposition.

152. The process of claim 151 wherein at least 0.05% by weight of the catalyst consists of at least one promoter.

153. The process of claim 152 wherein the promoter is more easily oxidized than the noble metal.

155

154. The process of claim 152 wherein the promoter comprises a metal selected from the group consisting of tin, bismuth, lead, cadmium, magnesium, manganese, nickel, aluminum, cobalt, titanium, antimony, selenium, iron,
5   rhenium, cerium, zinc, and zirconium.

155. The process of claim 152 wherein the promoter comprises tin.

156. The process of claim 152 wherein the promoter comprises iron.

157. The process of claim 152 wherein the promoter comprises titanium.

158. The process of claim 152 wherein at least two promoters are deposited at the surface of the non-graphitic carbon support.
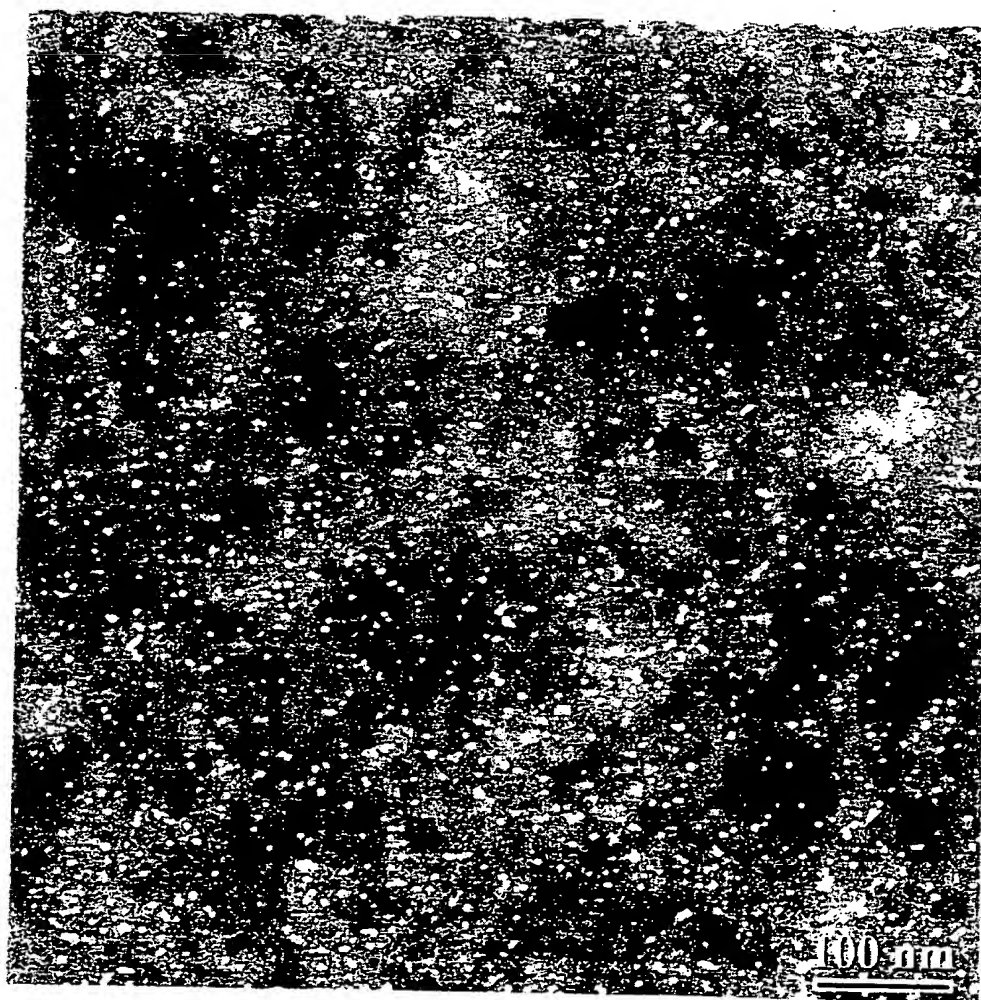
159. The process of claim 158 wherein the promoters comprise iron and tin.
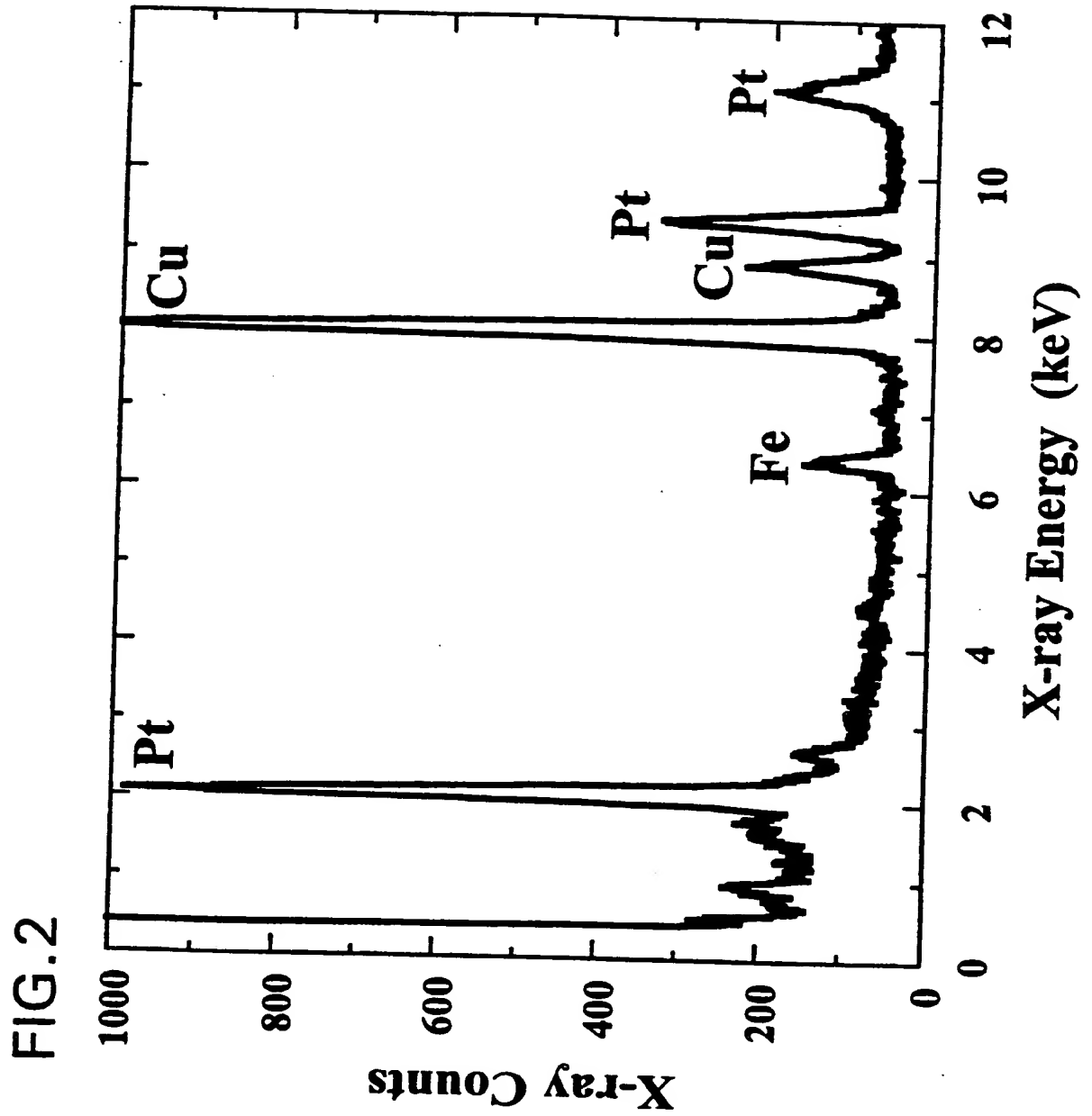
160. The process of claim 152 wherein noble metal atoms at the surface are alloyed with the promoter.

161. The process of claim 152 wherein a majority of the noble metal atoms at the surface are alloyed with the promoter.

162. The process of claim 152 wherein substantially all of the noble metals at the surface are alloyed with the promoter.

FIG. 1

FIG.2

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   B01J21/18   B01J23/40   C07F9/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   B01J   C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 601 715 A (ENGELHARD MIN & CHEM) 4 November 1981	68,69, 80-84, 86, 125-130, 151,152, 163-167
Y	see claim 1; examples 1-3	18-21, 43-46, 50-54, 57,88, 89, 100-106, 138-140
A	US 4 415 479 A (PUSKAS IMRE ET AL) 15 November 1983 --- -/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 June 1999	09/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Thion, M

Form PCT/ISA/210 (second sheet) (July 1992)

1

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 801 978 A (OSAKA GAS CO LTD ;MITSUBISHI HEAVY IND LTD (JP)) 22 October 1997 see claim 1	18-21, 43-46, 50-54, 57,88, 89, 100-106, 138-140, 346-350
A	EP 0 162 035 A (MONSANTO CO) 21 November 1985	
A	EP 0 595 124 A (BAYER AG) 4 May 1994	
X	US 3 950 402 A (FRANZ JOHN E) 13 April 1976 cited in the application see claim 1	333
Y		346-350

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 1601715	A	04-11-1981	AU	519502 B	10-12-1981
			AU	3375378 A	06-09-1979
			CA	1104112 A	30-06-1981
			DE	2809027 A	07-09-1978
			FR	2383882 A	13-10-1978
			JP	54056093 A	04-05-1979
US 4415479	A	15-11-1983	NONE		
EP 0801978	A	22-10-1997	CA	2206672 A	10-04-1997
			CN	1166142 A	26-11-1997
			WO	9712671 A	10-04-1997
EP 0162035	A	21-11-1985	US	4624937 A	25-11-1986
			AT	48766 T	15-01-1990
			AU	569794 B	18-02-1988
			AU	4221285 A	14-11-1985
			BR	8502200 A	14-01-1986
			CA	1244398 A	08-11-1988
			JP	1680242 C	13-07-1992
			JP	3046446 B	16-07-1991
			JP	60246328 A	06-12-1985
			MX	9102781 A	31-05-1994
			MX	165168 B	29-10-1986
			US	4696772 A	29-09-1987
EP 0595124	A	04-05-1994	DE	4236203 A	28-04-1994
			DE	59306174 D	22-05-1997
			JP	6199744 A	19-07-1994
			US	5410085 A	25-04-1995
US 3950402	A	13-04-1976	US	3954848 A	04-05-1976
			AU	5627773 A	05-12-1974
			BE	800238 A	30-11-1973
			BG	21212 A	20-03-1976
			CA	992093 A	29-06-1976
			CH	574968 A	30-04-1976
			CS	177133 B	29-07-1977
			DD	104303 A	05-03-1974
			DE	2327680 A	13-12-1973
			DE	2366060 A	06-10-1977
			DK	138951 B	20-11-1978
			EG	11140 A	15-08-1977
			FR	2186477 A	11-01-1974
			FR	2193831 A	22-02-1974
			GB	1432043 A	14-04-1976
			IE	37730 B	28-09-1977
			JP	49048620 A	11-05-1974
			JP	51011093 B	08-04-1976
			NL	7307449 A,B,	04-12-1973
			RO	62901 A	15-08-1977
			RO	66031 A	15-07-1980
			SE	404019 B	18-09-1978
			SE	407579 B	02-04-1979
			SE	7600415 A	16-01-1976
			YU	142773 A	18-06-1982
			YU	262880 A	30-06-1983
			AT	327946 B	25-02-1976

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 3950402 A		AT 477373 A		15-05-1975
		ZA 7303705 A		24-04-1974